

TEXTBOOKS OF PHYSICAL CHEMISTRY

EDITED BY SIR WILLIAM RAMSAY, K.C.B., D.Sc., F.R.S.

AND

F. G. DONNAN, C.B.E., M.A., Ph.D., F.I.C., F.R.S.

A SYSTEM OF PHYSICAL CHEMISTRY

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A SYSTEM OF PHYSICAL CHEMISTRY

WILLIAM C. McC. LEWIS, M.A.(R.U.I.), D.Sc.(Liv.), F.Inst.P.

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WITH DIAGRAMS

THIRD EDITION

IN THREE VOLUMES

VOLUME III

QUANTUM THEORY

• WITH CERTAIN APPENDICES BY JAMES RICE, M.A., A. McKEOWN
AND R. O. GRIFFITH, M.Sc.



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INTRODUCTORY NOTE.

IN this volume an attempt is made to deal with some physico-chemical applications of the principles of statistical mechanics. An account is first given of the application of what is now known as the classical statistical mechanics, more particularly to the problem of the energy content of substances and its variation with temperature, on the one hand, and to the problem of radiation on the other. It will be seen that in both these branches classical statistical mechanics makes it possible for us to advance very considerably beyond the limits set by the elementary kinetic theory employed in Volume I., but at the same time it will be found that the classical statistical mechanics does not furnish us with a complete and adequate basis for all the observed phenomena. It is therefore necessary to enlarge or modify the fundamental concepts of statistical mechanics, and it is precisely with this object in view that Planck has been led to introduce the idea of quanta. Planck's quantum theory is, therefore, properly speaking, a new or modified system of statistical mechanics, now usually referred to as quantum mechanics. It happens, however, that Planck was led to his revolutionary changes by considerations based upon the observed facts of radiation, and for this reason the term quantum theory of radiation is frequently employed. Radiation affords, as a matter of fact, one illustration, and a very striking one, of the applicability of the new mechanics. But even the success which has attended Planck's treatment of radiation problems would scarcely have sufficed to gain for his views that prominence which they now have, had it not been for the satisfactory explanation which his theory offers at the same time for the heat content of substances and the variation of the heat content with temperature. The idea of energy quanta has been applied in recent years to other types of physico-chemical phenomena, some of which will be considered. It will be assumed, in the treatment of the subject-matter dealt with in this volume, that

the reader is familiar with the principles of elementary kinetic theory and the principles of thermodynamics already discussed in Volumes I. and II. Such of these principles and results as may be required will be introduced therefore without further explanation.

It will be observed that there is a change of attitude in the mode of dealing with the experimental material in this volume as compared with the attitude adopted in the preceding volumes. The theoretical concepts made use of in Volumes I. and II. have become classical to a large extent, and the treatment resolves itself into a brief account of underlying principles followed by a systematic application of these principles to phenomena characteristic of systems which had attained equilibrium or were tending towards equilibrium. In the present volume, however, the underlying ideas, *i.e.* those involved in the quantum theory, have not as yet been fully accepted, at least in their present form. The position of the quantum theory is to a certain extent undefined. The physical significance of what is meant by a quantum of energy or, in a stricter sense, the quantum of action, is still vague. The present position has been summarised by Sir William Bragg in the words: "His [Planck's] hypothesis is not so much an attempt to explain as a focussing of all the difficulties into one; so that, if this master difficulty is overcome, a number of others melt away". In view of what has just been said, it will be readily appreciated that many of the experimental investigations referred to in the present volume have been carried out primarily with the object of testing the validity of the quantum hypothesis itself, and as this can be done most effectively by the intensive examination of individual fields of research, the information available at the present time is of a somewhat detached character. For this reason, therefore, relatively little stress is laid upon the system of classification already adopted in Volumes I. and II. The reader should be able to assign for himself any phenomenon or property under consideration to one or other of the two categories, *i.e.* the phenomenon is characteristic either of a system in steady equilibrium or of a system in process of change. Naturally with the progress of investigation it will become feasible ultimately to classify phenomena as has been done in the preceding volumes; but for the present the interest centres elsewhere, *viz.* on the validity of the underlying hypothesis itself. It is well that the reader should appreciate this state of affairs at the outset.

PREFACE TO THE THIRD EDITION OF VOLUME III.

FOR this edition Volume III. has been entirely revised and largely extended in order to make the treatment as comprehensive as possible.

In the case of a subject such as the physico-chemical aspect of the quantum theory, which is not only expanding rapidly but also undergoing modification, it is exceedingly difficult to carry out the process of selection and condensation in a satisfactory way. For criticisms and suggestions the author has pleasure in thanking various colleagues and friends, in particular Mr. James Rice, M.A., senior lecturer in Physics; Mr. A. McKeown, M.Sc., and Mr. R. O. Griffith, M.Sc., lecturers in Physical Chemistry of the University of Liverpool, who have contributed certain of the Appendices dealing with aspects of the subject with which they are specially conversant.

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CHAPTER I

Definitions—Probability—Statistical mechanics—Entropy and thermodynamics probability—Principle of equipartition of kinetic energy among degrees of freedom—Application of the equipartition principle to specific heats and radiation phenomena—Necessity of modifying the principle of equipartition.

DEFINITION OF STATISTICAL MECHANICS.

IN what we may call classical mechanics, developed in the first instance by Newton, we become acquainted with the concepts of mass, length, and time as the fundamental physical quantities, and from these we pass on to derived concepts, such as velocity, acceleration, force, and energy, by means of which we arrive at certain principles and laws which govern physical phenomena. We say that we have “explained” a physical or chemical phenomenon, when we can restate it in terms of mechanics; that is, when we can show that the phenomenon in question is to be anticipated on the basis of a number of mechanical principles logically applied. In Volume I. we have seen how the application of mechanics to the small discrete particles, which we recognise as molecules and atoms, leads to a reasonable explanation of many physico-chemical phenomena. We have restricted ourselves, however, hitherto by certain simplifying assumptions, *i.e.* we have dealt with systems of molecules as though all the molecules possessed exactly the same value for their velocity and therefore for their kinetic energy, throughout the given mass of material, an elementary gas, for example. It is known, however, that such an assumption is by no means true. We have already indicated this in Chap. I., Vol. I., when referring to the distribution of velocities among a large number of gas molecules in terms of Maxwell’s distribution law. It is true that all our experimental measurements deal with average effects, and hence by regarding every molecule as in an average state and applying the principles of mechanics, we are able to arrive at a number of very important and useful conclusions in terms of the elementary kinetic theory, for which we find experimental evidence.

This mode of treatment, however, has its limitations. Certain problems present themselves which we are quite unable to solve on the basis of the elementary kinetic theory. We have already met a number of these in Volume II., and have shown how they may be dealt with from the standpoint of thermodynamics. By way of illustration we may cite: the relation between the lowering of vapour pressure, lowering of freezing point, and rise of boiling point of a liquid as a result of

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dissolving some substance in the liquid; the variation of the pressure of saturated vapour with temperature in terms of the latent heat of vaporisation; the variation of the equilibrium constant of a chemical reaction with temperature and pressure; the electromotive force of reversible cells; the relation between the heat of reaction and the chemical affinity of the process.

The laws of thermodynamics are not, however, in the first place, mechanical laws—though we shall see later that the second law possesses a statistical mechanical basis—but are founded essentially upon experience; they are taken to be true, because no phenomenon or process in nature contradicts them. The characteristic feature of thermodynamical treatment is, as we have already seen, that the results obtained involve no assumption regarding the molecular structure of the system under consideration. Thermodynamical deductions are therefore perfectly general, in the sense that they hold good quite apart from specific molecular theories. It is important to point out that mechanics likewise furnishes a general mode of treatment, known as *generalised dynamics*, by which certain physico-chemical results may be obtained, the line of reasoning followed being to a certain extent analogous to thermodynamic reasoning in that no particular assumption is made regarding the molecular structure and molecular properties of the system investigated. We treat the system as a whole and do not attempt to deal with each molecule individually.

The best account of the applications of generalised dynamics to physico-chemical problems is that of Sir J. J. Thomson, in his book *Applications of Dynamics to Physics and Chemistry*. Among the problems solved by this method are: the process of evaporation (including the effect of electric charge upon the vapour pressure), the effect of an inert gas upon the value of the saturated vapour pressure; certain properties of dilute solutions, such as the lowering of the vapour pressure of the solvent by addition of solute, and the lowering of the freezing point by the solute; the deduction of the law of mass action, as expressed in the equilibrium constant, the equilibrium constant being shown to be an explicit function of the temperature; the principle of mobile equilibrium; the effect of pressure upon the freezing point of a pure liquid, and the effect of pressure upon the solubility of one substance in another; the phenomenon of adsorption; the relation between the electromotive force and “the chemical change producing it”; and other problems.

It is evident from this enumeration that the methods of generalised dynamics are of wide applicability. No attempt is made, however, to pursue this method in the present volume. Suffice it to say that generalised dynamics is based upon a general principle embodied in Hamilton's and Lagrange's functions. These “hardly require a more detailed knowledge of the structure of the system to which they are applied than the conservation of energy—the first law of thermodynamics—itsself, and yet are capable of completely determining the motion of the system”. Thomson compares the thermodynamical

method of treatment with that of generalised dynamics, and points out that the disadvantage of the latter compared with the former, lies in the fact that, "the results are expressed in terms of dynamical quantities, such as energy, momentum, or velocity, and so require further knowledge before we can translate them in terms of the physical quantities we wish to measure, such as intensity of a current, temperature, and so on; a knowledge which in all cases we do not possess. The second law of thermodynamics, on the other hand, being based on experience, does not involve any quantity which cannot be measured in the laboratory."

It is evident that generalised dynamics and thermodynamics have the great merit in common that they are essentially generalisations, and their application does not require any specialised information such as that involved in the molecular kinetic theory. What has been said therefore in Volume II. in regard to the advantage which this quality confers in the case of thermodynamics applies to much the same extent to generalised dynamics. The same disadvantage manifests itself of course, *viz.* that we do not get any clearer picture of the phenomenon in question in terms of the molecules taking part therein.

It is very necessary, however, to attempt to deal with processes which are essentially molecular in terms of the molecules themselves. The difficulty lies in the fact that when a system consists of a very large number of individuals (*e.g.* the molecules in a gas), it is quite impossible to follow out the extremely complicated path pursued by each single individual. In order to advance beyond the mode of treatment employed in the elementary kinetic theory of Volume I.—in which we got round the difficulty here presented by making the certainly untrue assumption that all molecules were identical in all respects—it is necessary to proceed in quite a different manner by introducing a new idea into mechanics which will enable us to deal with physical and chemical problems in a more exact and logical way. This new idea—the introduction of which into mechanics we owe principally to Maxwell and to Boltzmann—is embodied in the theory of Probability. When we bring probability considerations into mechanics we arrive at a mode of treatment known as *statistical mechanics*.¹ By treating molecular processes from the standpoint of statistical mechanics we are able to take account of the fact that all the molecules are not really identical but differ from one another in general in respect of velocity, direction, and energy content. The results obtained are indeed average results—as they must be if they are to be amenable to experimental test—but such results represent the combined effect of all the molecules present, due allowance being made for the lack of equality in the actual contribution made by each individual molecule to the total observed effect. This must not be taken as meaning that we have to calculate the particular position, velocity, and energy of each individual molecule at various intervals of time. This, as already pointed out, would be quite impossible. Instead, we

¹ For an account of this method of treatment, the reader is referred to the forthcoming work on *General Dynamics and Statistical Mechanics*, by J. Rice, M.A.

take advantage of the fact that the number of the molecules involved in any system with which we are concerned in physics or chemistry is so enormous that we are justified in dealing with these aggregations of molecules in a statistical manner, by introducing the principle of probability or chance into the mechanics of the process considered.

It is not proposed to attempt to give a systematic account of what may be called the principles of statistical mechanics. We are concerned mainly with one such principle, known as the principle of equipartition of kinetic energy among degrees of freedom. We shall state and apply this principle later. For the present it is necessary to familiarise ourselves with the idea of probability.

PROBABILITY.

In a purely algebraic sense probability may be defined as follows: If an event can occur in a ways and fail in b ways, each of these ways being equally likely, then the chance or probability of its occurring is $a/(a+b)$, and the chance or probability of its failing to occur is $b/(a+b)$. The sum of these two terms is necessarily unity, for the sum of the two probabilities covers all eventualities, *i.e.* the event must either happen or fail, and the sum represents certainty. It follows that mathematical probability is a fractional quantity which may be small or large, but can never exceed unity,¹ *i.e.* certainty. We may illustrate the idea by one or two examples. Suppose we have equal numbers of black and white balls inside a bag, the bag being well shaken so as to destroy any possible regularity or ordered arrangement of the balls, what is the probability or chance that, say, a white ball will be drawn from the bag? It is evident that the chance of drawing a white is the same as that of drawing a black. In other words, the probability is one half, for here $a = b$ when a is the number of white and b the number of black balls, and $a/(a+b) = 0.5 = b/(a+b)$. It is evident that in the limit, if b becomes very small compared with a , the probability of drawing a white increases almost to a certainty, *i.e.* the fraction $a/(a+b)$ is nearly unity. We are here considering the probability of a single event occurring. Let us now consider the probability that two independent events may occur *simultaneously*. The probability in such a case is easily shown² to be the *product* of the probabilities of the separate events. That is, if the probability of the first event is P_1 , and that of the second is P_2 , then the probability P of both events occurring simultaneously is $P = P_1 P_2$. Thus, if we have two bags, each containing a white balls and b black ones, the chance of drawing a single white from one bag is P_1 , where $P_1 = a/(a+b)$, and the chance of drawing, say, a black ball from the other bag is P_2 , where $P_2 = b/(a+b)$. The chance of drawing a white ball from the first bag

¹ Whilst this is true of mathematical probability we shall find later that there is a quantity to which the term "thermodynamic probability" has been given, this quantity being in general a large integral number.

² Cf., for example, Hall and Knight's *Algebra*.

and simultaneously a black ball from the second bag is P where $P = ab/(a+b)^2$. This simple relation between the probabilities of two separate events and the probability that both will occur simultaneously is of great importance, and will be made use of later. Let us now consider one or two cases which possess a more distinctly chemical character.

The first which we shall take is the elementary deduction of the law of mass action given in Vol. I., Chap. III. Suppose we have a gaseous system containing n_a molecules of the substance A, and n_b molecules of the substance B. The probability of a collision between a single molecule of A and a single molecule of B is the product of the fractional concentration of each, for a collision is analogous to two events happening simultaneously, which we have just seen depends upon the product of two single chances, each of which is represented by the fractional concentration of A and B respectively.

We might regard the problem in the following way. Suppose that v is the molecular volume, *i.e.* the actual volume "occupied" by or allotted to any single molecule of A or B in the mixture. Let V be the total volume. Then, $V = (n_a + n_b)v$. Suppose for the moment that there is only one molecule of A present. Then the chance that this molecule would occupy a given volume v at a given instant of time would be the ratio of this volume to the total volume, *i.e.* the ratio v/V or $1/(n_a + n_b)$. Since there are n_a molecules of the substance A actually present, the chance that *any one* of them occupies a certain "position" or space v is given by the ratio $n_a/(n_a + n_b)$. This term is likewise the fractional concentration of the substance A. The chance that any B molecule occupies the same position is given by the expression $n_b/(n_a + n_b)$. If a molecule of A and a molecule of B occupy the same position together, this is equivalent to a collision, and hence the chance of a collision is the product of the fractional concentrations.

If the reaction required say two molecules of A to meet one molecule of B simultaneously the chance of this occurring is $\left(\frac{n_a}{n_a + n_b}\right)^2 \cdot \frac{n_b}{n_a + n_b}$ which finally takes the form: rate of collision $= kC_a^2 \cdot C_b$, for the total volume is proportional to the total number of molecules present.

These simple probability ideas may also be used to account for the influence exerted upon the collision frequency by the fact that in actual gaseous systems the molecules possess volume. Thus if r is the radius of a molecule, and l the average distance between two molecules, then when a molecule moves over a distance l it sweeps out a cylinder the cross-section of which is πr^2 and the length l . The volume of this cylinder is therefore $\pi r^2 l$. Each molecule has, on the average, a free space allotted to it which is a cube of volume l^3 . Hence, as far as the radius affects the question, the chance of one molecule encountering another is $\pi r^2 l/l^3$ or $\pi r^2/l^2$. If the average velocity is u , the time of a journey between two successive collisions is l/u . Hence the number of encounters per second is $(u/l) \times$ chance of collision $= u\pi r^2/l^3$. This

quantity is obviously a constant for a particular gas at constant temperature, and hence is really included in the proportionality factor or velocity constant k .

Another illustration of the application of probability considerations is afforded by the phenomenon of coagulation of colloids by electrolytes (*cf.* Whetham, *Phil. Mag.* [v.], **48**, 474 (1899)). It is supposed that the coagulation is due solely to the neutralisation of the electrical charge of the colloid, and that one trivalent ion is exactly equivalent to 1.5 divalent ions, or to three univalent ions as far as coagulating efficiency is concerned. This is, of course, too simple an assumption, as we have already seen in the criticism of Schultze's rule (Vol. II., Chap. VIII.). Adopting this simple view of the effect, however, Whetham has shown how the numerical values obtained experimentally may be accounted for approximately. The coagulating power of an ion is defined as the reciprocal of the number of gram-equivalents of the ion which are just capable of bringing about coagulation of a given quantity of colloid. Linder and Picton found that negatively charged colloidal arsenic sulphide could be coagulated by tri-, di-, or uni-valent cations, the relative coagulating powers being in the ratios—

$$1023 : 35 : 1.$$

Let us suppose that in order to produce coagulation a certain minimum electric charge has to be brought into contact with the colloidal particle, and that such conjunctions must occur with a certain minimum frequency throughout the solution. We shall get equal charges by the conjunction of $2n$ trivalent ions, or $3n$ divalent ions, or $6n$ univalent ions, where n is any whole number. In a solution where ions are moving freely the probability that an ion is at any instant at a certain position is represented by a fraction which is proportional to the ratio between the volume occupied by the sphere of influence of the ion and the total volume of the solution. The probability is therefore proportional to the concentration of the ion, and may be written as (Ac) , where A is any constant. The probability that two such ions are present together is $(Ac)^2$, and the chance that n such ions are present simultaneously at the position is $(Ac)^n$. Let us suppose that three solutions containing respectively tri-, di-, and uni-valent ions at concentrations C_3 , C_2 , and C_1 possess exactly the same coagulating power upon a given amount of a given colloid. Then, since the coagulating power is the same in these three cases—

$$A^{2n}C_3^{2n} = A^{3n}C_2^{3n} = A^{6n}C_1^{6n} = \text{a constant} = B.$$

Hence, the critical concentration of the trivalent ions is given by—

$$C_3 = \frac{B^{\frac{1}{2n}}}{A}$$

$$\text{and similarly } C_2 = \frac{B^{\frac{1}{3n}}}{A} \text{ and } C_1 = \frac{B^{\frac{1}{6n}}}{A}.$$

The ratios in which these three concentrations stand to one another are—

$$C_1 : C_2 : C_3 = B^{\frac{1}{6n}} : B^{\frac{1}{3n}} : B^{\frac{1}{2n}}$$

$$= 1 : B^{\frac{1}{6n}} : B^{\frac{1}{3n}}.$$

Putting $B^{\frac{1}{6n}} = 1/x$, the ratios can be written—

$$1 : 1/x : 1/x^2.$$

These represent numbers which indicate relative concentrations of equal coagulating power. Hence the relative coagulating powers P_1, P_2, P_3 of *equal* concentrations of these three ions are given by the reciprocal of the above numbers. That is—

$$P_1 : P_2 : P_3 = 1 : x : x^2.$$

The value of x , which depends upon a number of unknown factors characteristic of the colloid considered, cannot be found on *a priori* grounds. If we take Linder and Picton's experiments into account and set $x = 32$, we get for the relative coagulating powers of univalent, divalent, and trivalent ions respectively, the values $1 : 32 : 1024$. It will be seen that these numbers are of quite the same order of magnitude as those observed. Whetham predicted on this basis that the coagulating power of a tetravalent ion on the above colloid should be a large number, approximately 33000. Recent measurements have corroborated this result in so far as an extraordinarily large coagulating power is actually obtained.

The Law of Error.—It is a familiar fact in physico-chemical measurements that repetitions of a certain measurement give rise to a series of numbers which are not identical. The variations we speak of as experimental errors. The measurements are as likely to be too high as too low, that is, the errors are as often positive as negative, provided we make a very large number of determinations. (It is assumed that there is no systematic error in the apparatus or in the method of measurement.) The treatment of such results so as to obtain the most probable result, *i.e.* the most accurate determination, is a further illustration of the application of the theory of probability, somewhat more complex in nature than that hitherto considered.

Thus, it is possible to construct a probability curve, by means of the probability equation given below, which has been found to agree closely with the actual results obtained in a series of experimental determinations of a given quantity. Examples will be found in a text-book of mathematics, *e.g.* Mellor's *Higher Mathematics*. The large majority of the readings will fall very closely together, *i.e.* they will not be far removed from the true result, a smaller number of readings will be farther away on either side of the true result, and only a very

small number will be much to one side or the other. This distribution of values may be represented by an expression of the form—

This is known as the normal law of errors. The curve is shown in Fig. 1. x denotes the error and y the probability of its occurrence. As x increases numerically, positively, or negatively, y decreases rapidly, and when x becomes large y becomes vanishingly small. It will be observed that the curve is symmetrical.

Maxwell's Law.—Maxwell has applied the principle of probability to the problem of the distribution of velocities among the molecules of a gas, the gas being in a condition of statistical equilibrium at a uniform temperature throughout. A gas is to be regarded as a molecular chaos, the speed of any molecule varying from zero to infinity, its in-

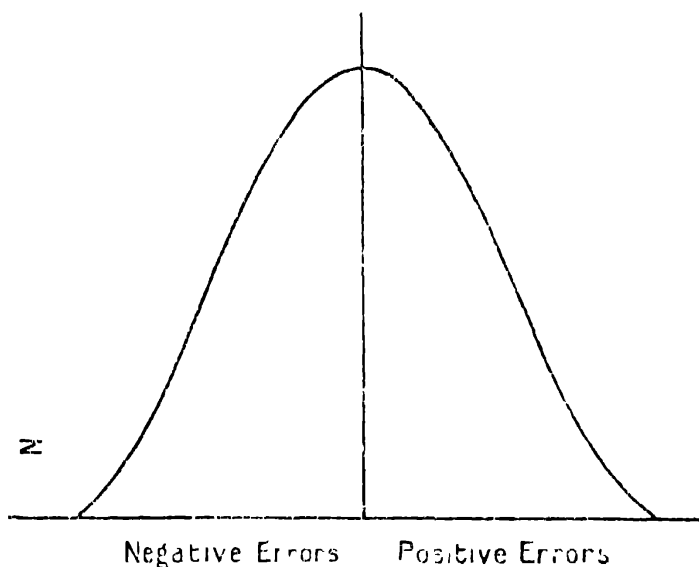


FIG. 1.

stantaneous value being the result of chance collisions with its neighbours. Although all values are theoretically possible for the speed of a molecule, it is found that in a system containing a large number of molecules, there are very few possessing either very great or very small speeds. The majority of the molecules possess speeds which lie within relatively restricted limits. A numerical illustration taken from Meyer's *Kinetic Theory of Gases* is given in Appendix I.

There are, as a matter of fact, two ways of expressing Maxwell's law of distribution. One of these ways has already been stated in Chap. I., Vol. I. This way of expressing the law may be put in the form—

$$dn = \text{constant} \times N \times e^{-3c^2/\bar{c}^2} \cdot c^2 \cdot dc$$

where N is the total number of molecules in the system, and dn is the number whose speeds lie between the limits c and $c + dc$. It is to be clearly understood that the speed here referred to is simply a velocity

magnitude, and no restriction has been introduced as to direction of motion. The term c is known as the root-mean-square speed (or *r-m-s* speed). At a given temperature the system is characterised by a certain mean or average kinetic energy of its molecules, which is maintained as long as the temperature is maintained constant. This average kinetic energy may be written as $\frac{1}{2}Nmc^2$, where $\bar{c}^2$ is the sum of the squares of the velocities of all the molecules at any given instant divided by N . This *r-m-s* speed is not the same thing as the mean or average speed, which is simply the sum of all the velocities divided by N , though the two quantities are not very different numerically. The above way of expressing Maxwell's law, *i.e.* the above expression, is of the general form: $y = Ae^{-x^2}$, which, it is to be observed, is *not* identical with the normal law of errors. The resulting curve is, in fact, not symmetrical. The alternative mode of expressing Maxwell's law wherein the curve is symmetrical, and the distinction between the two modes, is considered in Appendix I.

Maxwell's law expresses the distribution of velocities as a *continuous* function of the number of molecules present. That is, the speed of one molecule may differ by any amount (down to the infinitesimally small) from the speed of any other molecule. When we come to consider the quantum theory we shall find continuous functions replaced by discontinuous ones, *i.e.* abrupt changes in finite small steps in place of gradual change in infinitely small steps.¹

It will be observed that Maxwell's expression involves the squares of velocities. Since the kinetic energy of a molecule depends upon the square of its velocity, it should be possible, on similar lines, to express the distribution of kinetic energy amongst the molecules constituting a gas system. If we denote by dn the number of molecules which possess kinetic energy lying between the limits E and $E + dE$, it can be shown that at a given temperature—

$$dn = \text{constant} \times N \times e^{-1/kT} \cdot E^{\frac{1}{2}} \cdot dE$$

where N is the total number of molecules, and k the gas constant per molecule (*i.e.* $k = R/N_0$, where R is the gas constant per gram-molecule, and N_0 is the number of molecules in 1 gram-molecule).

Further, potential energy of molecules may be considered as distributed in an analogous manner. We are here considering the potential energy of a molecule, free from intermolecular forces (as in the case of a perfect gas), the molecules being placed, however, in a field of force and the potential energy being due to this field of force, which might be conceived of as originating in some external body. A good example is the earth's gravitational field which acts on a column

¹ This statement must not be taken as meaning that the distribution of kinetic energy of *translation* takes place in the discontinuous manner postulated by the quantum theory. The quantum theory applies only to energy of the vibrational or rotational type, *i.e.* motion with respect to some fixed centre of gravity. Free translational motion—such as that considered above—must be treated in a continuous manner, the velocity being capable of changing by an *infinitely* small amount.

of gas in such a way that the molecules are more dense in the lower portion of the column than in the upper. Denoting potential energy by W , we can state that the number of molecules, the potential energy of which lies between W and $W + dW$, is given by—

$$dn = \text{constant} \times N \times e^{-w/kT} \cdot dW.$$

We can integrate this to obtain the number n_1 of molecules of a perfect gas (in equilibrium in a field of force at a uniform temperature) which possess potential energy W_1 , that is all values from zero up to W_1 .

If the total number of molecules in the system be N , the expression is

$$n_1 = N(1 - e^{-w_1/kT}).$$

If we introduce the Avogadro constant N_0 , i.e. the number of molecules in one gram-molecule, the above expression becomes—

$$n_1 = N(1 - e^{-N_0 w_1/RT}),$$

where R is the gas constant per gram-molecule.

It follows from this that the number of molecules which possess potential energy between W_1 and infinity is $(1 - n_1)$ which is equal to

$$Ne^{-w_1/kT} \text{ or } Ne^{-N_0 w_1/RT}.$$

Distribution of Molecular Velocities and Temperature.—On the kinetic theory it is to be expected that the temperature of a gas should be expressible in purely mechanical terms. We are already familiar with the concept that temperature is measured by the kinetic energy of the molecules. In view of the distribution of velocities and therefore of kinetic energy, among molecules, as expressed in Maxwell's law, it is evident that the kinetic energy of a given individual molecule may be very different from that possessed by another molecule of the same system. Further, the kinetic energy of one and the same molecule varies from moment to moment as a result of collisions. The temperature of the system—measured in the ordinary way, by means of a thermometer—is a perfectly definite quantity for the gas system as a whole in the steady state. The temperature, in fact, is determined by the average kinetic energy. It is therefore meaningless to speak of the temperature of a single molecule in a gas. Temperature is essentially a statistical effect due to the presence of a large number of molecules each contributing its own share to the total effect. Two independent systems are at the same temperature when the average kinetic energy of each is the same. This is true whether the systems be gaseous, liquid, or solid, homogeneous or heterogeneous.

It will be appreciated at the same time that pressure is likewise a statistical effect. A single gas molecule cannot be conceived of as exerting observable pressure, though each molecule exerts a certain force against the walls of the containing vessel, the total effects of which, when numerous molecules take part, is manifested as a uniform gas pressure.

ENTROPY AND THERMODYNAMIC PROBABILITY.

It is proposed to indicate how the second law of thermodynamics can be deduced on the basis of statistical mechanics. This was first demonstrated by Boltzmann. Hitherto we have regarded the second law as a law of experience, its validity depending upon the fact that no contradiction to it has been met with in nature. It is important to see that this law possesses at the same time a mechanical basis. The demonstration consists in showing the connection between the entropy of a system—the concept of entropy involving necessarily the concept of the second law—and a statistical quantity known as the *thermodynamic probability* of the system.

It is necessary to recall first of all what is meant by thermodynamical equilibrium, as stated in terms of entropy, that is, as stated in terms of the second law. Planck's definition of such equilibrium is as follows (*cf.* Planck, *Theory of Heat Radiation*, English ed., p. 22): "A system of bodies of arbitrary nature, shape, and position, which is at rest and is surrounded by a rigid cover impermeable to heat, will, no matter what its initial state may be, pass in the course of time into a permanent state in which the temperature of all bodies in the system is the same. This is the state of thermodynamic equilibrium, in which the entropy of the system has the maximum value, compatible with the total energy of the system as fixed by the initial conditions. This state being reached no further increase in entropy is possible."

We know that heat, from the kinetic molecular point of view, is represented by the kinetic energy of the molecules of a system, the molecules moving about in a completely chaotic manner as a result of collisions. Owing to collisions any ordered arrangement which the molecules might be conceived of as possessing initially would be quickly annulled, and completely disordered distribution, both as to position and to molecular velocities, would ensue. This represents the direction of change in any spontaneous or naturally occurring process. That is, from the molecular standpoint a system always changes from an ordered to a chaotic state, and the change will go on until the molecular motion has become as disordered as possible. When this stage is reached, there is no longer any reason for further change. When equilibrium is reached the system has at the same time reached a maximum disorder or "mixed-up-ness". This involves the idea that a system in equilibrium possesses a maximum value of the probability of the state, the probability here referred to dealing with possible modes of molecular arrangement and velocity. We may call this the thermodynamic probability.

According to Boltzmann the thermodynamic probability of an ideal monatomic gas is a number which denotes by how many times or by how much the actual state of a gas system is more probable than a state of the same gas system (*i.e.* possessing the same total energy and volume) in which the molecules are equally spaced and all possess the same velocity. This "standard" state represents perfect order or arrangement of the molecules. It is of course never realised in practice

owing to the disorder brought about as a result of collisions. The standard state represents the stage furthest away from the equilibrium state finally attained by the gas, in which final state the system is completely chaotic. The probability of disorder is very much greater than the probability of complete order.

The thermodynamic probability of this "standard" state (that is the probability of complete order) is taken to be unity. It follows therefore that the thermodynamic probability of a real equilibrium state is an integral number usually much greater than unity. Thermodynamic probability differs therefore from mathematical probability in that the latter is always a fractional quantity, *i.e.* it denotes the ratio of the number of favourable cases to the total number of possible cases. Thermodynamic probability is proportional to, but is not identical with, mathematical probability.

It has just been stated that a system in equilibrium possesses a distribution or arrangement which is characterised by a maximum value for the thermodynamical probability of the state. It is necessary before going further to give a somewhat more concrete idea of what we mean by states or arrangements and the probability of arrangements. Let us leave the problem of molecules and turn to a very simple kind of system which can undergo various arrangements.

Let us suppose that we have two squares or areas denoted by the symbols I and II, and further let us suppose that we have five letters, *a, b, c, d, e*, and we wish to distribute or arrange these letters between the squares in every possible way. It is evident that all possible ways are included in the following :—

		II.	Nature of Arrangement.
<i>First arrangement .—</i>			
1st way of arranging the letters is	abcde	—	All letters in I none in II.
<i>Second arrangement :—</i>			
2nd way of arranging the letters is	abcd	e	Four letters in square I ; one letter in II. There are five ways of producing this arrangement or distribution.
3rd " " " "	abce	d	
4th " " " "	abde	c	
5th " " " "	acde	b	
6th " " " "	bede	a	
<i>Third arrangement —</i>			
7th way of arranging the letters is	abc	de	Three letters in square I ; two letters in square II. There are ten ways of producing this arrangement or distribution.
8th " "	abd	ce	
9th " "	acd	be	
10th " "	bcd	ae	
11th " "	abc	cd	
12th " "	ace	bd	
13th " "	bce	ad	
14th " "	ade	bc	
15th " "	bde	ac	
16th " "	cde	ab	

We now begin with an arrangement similar to the first, but place all the five letters in square II and none in square I. Similarly we can interchange squares I and II in the other two arrangements, so that in all, there are six *arrangements* possible in this system, and in all, thirty-two different *ways* in which these six arrangements or distributions may be carried out. Each of these *ways* is analogous to a "complexion" on Boltzmann's nomenclature. Every way or complexion is to be regarded as equally probable. It is very necessary to distinguish between arrangement or distribution and complexion. Thus in the first case, the arrangement is five letters in square I, none in square II. There is only one way or complexion of doing this. In the second arrangement, which consists of four letters in square I and one letter in square II, there are five ways or complexions of doing this. It is simply a question of combinations. Thus there are five letters to be divided in such a way that four are in one square, one in another square. The number of possible ways of doing this particular

distribution is $\frac{5!}{4!1!} = 5$. In the third arrangement or distribution

we have to distribute the letters so that there are always three in square I and two in square II. There are ten ways or complexions corresponding to this single distribution. This number is given by

$\frac{5!}{3!2!} = 10$. Note that the problem is not *which* letters are in the squares, but how *many* different ways can they be divided to correspond with any particular arrangement, such as three letters in one square, two in the other.

• If instead of five letters we had N letters and divided them between two squares, in such a way that n letters are in square I and $N-n$ letters in square II, the possible ways or complexions possible to this particular distribution are—

$$\frac{N!}{n!(N-n)!}$$

If, instead of two squares, we had m squares, the total number of complexions in a particular distribution would be given by—

$$\frac{N!}{n_1! n_2! n_3! \dots n_m!}$$

where $n_1 + n_2 + n_3 + \dots + n_m = N$.

To return to the simple case of five letters and two spaces. We have seen that there are six possible arrangements or distributions, *viz.*, (5) (0); (4) (1); (3) (2); (0) (5); (1) (4); (2) (3). Each of these arrangements has its own number of ways or complexions. Thus for arrangement (5) (0), the number of complexions is one. For arrangement (4) (1), the number of complexions is five; for arrangement (3) (2), the number of complexions is ten. Similar numbers of

complexions are found in the remaining arrangements or distributions. It is evident that the arrangement (3) (2) has the same number of complexions as the arrangement (2) (3), and that either of these two arrangements or distributions possesses the *maximum number* of complexions. But the number of complexions is identical with the thermodynamic probability of the particular distribution under consideration. Either of the systems (3) (2) or (2) (3) possesses the *maximum probability*. Either distribution represents therefore the equilibrium distribution. The distribution (3) (2) or (2) (3) is the most likely distribution of five letters scattered at random between two squares. The equilibrium distribution in the above system is ten times more likely than the distribution (5) (0) or the distribution (0) (5), for the latter only possesses one complexion whilst the equilibrium distribution possesses ten.

The choice of five letters has somewhat obscured an important point in that we are led to two distributions of equal maximum probability. To find a closer analogue to the actual case of molecular systems containing an enormous number of molecules it is better to choose as the simplest model the distributions of six letters between two squares. With this system we have the following distributions and corresponding complexion-number for each distribution :—

			Complexion- Number
1st distribution or arrangement	6 letters in I	0 letters in II	I
2nd " "	5 " "	1 " "	6
3rd " "	4 " "	2 " "	15
4th " "	3 " "	3 " "	20
5th " "	2 " "	4 " "	15
6th " "	1 " "	5 " "	6
7th " "	0 " "	6 " "	1
Total number of complexions = 64			

The single arrangement or distribution which contains the maximum number of complexions is that represented by three letters in each square. This distribution has therefore the maximum probability, *i.e.* it is the one most likely to occur if six letters be scattered at random over two squares. This distribution is consequently the "equilibrium" distribution of the constituents of this system which consists of six letters. •

Now let us apply this idea to a system of molecules. In this case also that distribution or arrangement which has the greatest number of complexions or ways is the most probable arrangement, its degree of probability, or simply its probability, being measured numerically by the number of complexions possible to it. The most probable distribution is the equilibrium distribution or state or condition of the system. A system changes in the sense that it tends to approach and

finally reach an equilibrium state. In this state the number of possible complexions is a maximum, *i.e.* greater than the number of complexions in any other distribution of the constituents of the system. A maximum number of complexions is identical with the idea of maximum disorder or maximum molecular chaos.

In all spontaneous processes the thermodynamical probability tends to reach a maximum. But on purely thermodynamical grounds we know that in spontaneous processes the entropy of a system tends towards a maximum value consistent with the total energy of the system. It follows, therefore, that there must be some close relation between the thermodynamical probability of a state and the entropy of the state. We can express this by writing—

$$S = F(w),$$

where S is the entropy of the system in any state, not necessarily the equilibrium state, w the thermodynamic probability of the same state, and F is some function still to be determined. To determine the nature of F , let us suppose that we have two independent systems, each one in a definite state, the entropy of the first being denoted by S_1 , the probability of the state or arrangement of the first system being w_1 , the entropy of the second system being S_2 , and the probability of the state of the second system being w_2 . We then have the relations—

$$\begin{aligned} S_1 &= F(w_1) \\ S_2 &= F(w_2). \end{aligned}$$

The total entropy S of the two systems taken together is the sum of the separate entropies. That is—

$$S = S_1 + S_2 = F(w_1) + F(w_2).$$

Since the particular state or arrangement of the first system can be realised by selecting any *one* of the w_1 complexions (contained in or characteristic of that arrangement or state) and similarly for the second system, it follows that the state or arrangement of the combined system can be realised by selecting any one of the w_1 complexions of the first and combining them with the w_2 complexions of the second. That is, the compound arrangement is obtained by selecting any one of the w_1 and w_2 complexions. That is, the probability w of the compound state is $w_1 \times w_2$.

But for the compound system we have the relation: $S = F(w)$. Hence from the above we get: $S = F(w_1 \cdot w_2)$. But we have already seen that $S = F(w_1) + F(w_2)$. Hence, $F(w_1 \cdot w_2) = F(w_1) + F(w_2)$.

The only function which will satisfy this relation is the logarithmic one, *i.e.* $\log xy = \log x + \log y$.

Hence, the connection between the thermodynamic probability and the entropy of a system is given by the relation:—

$$\begin{aligned} \text{Entropy} &\propto \log_e \text{Probability} \\ \text{or} \quad S &= k \log_e W, \end{aligned}$$

where k is a constant independent of the chemical nature of the system and independent of the conditions under which the system is examined. A more general form of the above expression is—

$$S = k \log W + \text{constant.}$$

We have now to find out the significance of the universal constant k .

To do this we make use of a statistical expression arrived at by Boltzmann for the entropy of a perfect monatomic gas. A monatomic gas is one in which the total or internal energy U is due entirely to the kinetic energy of the molecules. Boltzmann's expression is—

$$S = \frac{3}{2}kN \log U + kN \log v + K$$

where U and k are defined above, N is the number of molecules in the system, v the volume of the system, and K is a constant independent of the energy and volume but involving the number and mass of the molecules. It has already been shown in Volume II. that the following purely thermodynamical relation holds good:—

$$\frac{\partial S}{\partial T} = \frac{1}{T} \frac{\partial U}{\partial T}$$

Differentiating Boltzmann's expression for the entropy of a perfect monatomic gas we obtain:—

$$\frac{\partial S}{\partial T} = \frac{3}{2}kN \frac{1}{U} \frac{\partial U}{\partial T}$$

Hence $U = \frac{3}{2}kNT$.

If N be taken as denoting the number of molecules in one gram-molecule, then U denotes the total energy of one gram-molecule of monatomic gas.

But we have already seen (Vol. I.) that in the case of a perfect gas, the total *kinetic* energy of all the molecules forming one gram-molecule is $\frac{3}{2}RT$, where R is the gas constant per gram-molecule. Further, in the case of a monatomic gas the energy, as will be shown later, is entirely kinetic. Hence for one gram-molecule of a monatomic gas: $U = \frac{3}{2}RT$.

It follows, therefore, that—

$$Nk = R,$$

or k is the gas constant per single molecule.

Further, in the case of a perfect gas, $\frac{3}{2}R = C_v$ where C_v is the gram-molecular heat at constant volume. Hence the equation of Boltzmann for the monatomic gas becomes—

$$S = C_v \log T + R \log v + K_1$$

where S now denotes the entropy of one gram-molecule. This expression is in complete agreement with that already deduced in Volume II. on thermodynamical grounds, *viz.*:—

$$S = C_v \log T + R \log v + S_1$$

If we identify S_1 with K_1 . This constant represents the value of the entropy under certain conditions. On purely thermodynamical grounds it is legitimate to consider that the entropy may assume in general any value whatsoever, positive or negative, and that therefore all that we can measure is the *change* in entropy resulting from a physical or chemical process. It will be pointed out later in dealing with Nernst's Heat Theorem that, according to Planck, the Heat Theorem itself is equivalent to regarding the entropy of all substances as zero at the absolute zero of temperature, and possessing therefore a positive value at all other temperatures.¹ This gives us a starting point from which to calculate not only change in entropy but its absolute value under given conditions. This likewise agrees with the simplified expression: $S = k \log W$ in which W has been defined as a quantity greater than unity, and consequently S is essentially positive. Of course, if we retain the constant in the expression: $S = k \log W + \text{constant}$, the value of S may be positive or negative, depending upon the magnitude and sign of the integration constant whether W itself is greater than unity or not. Classical statistical mechanics, which did not attempt to assign any particular limit to the value of the entropy, is represented by the above expression. If we assume with Planck that the integration constant is zero, and remembering that W as defined above is greater than unity, it follows that S is a positive term becoming zero at absolute zero. This is equivalent to assuming the quantum hypothesis.

The general position which we have now reached as a result of the considerations dealt with in this section may be summarised as follows:—

The second law of thermodynamics, regarded as a law of experience, states that, whilst work may always be completely converted into heat, heat on the other hand cannot be completely converted into work. In other words, all natural spontaneous processes are thermodynamically irreversible. In mechanics we deal only with reversible processes, and from the standpoint of mechanics alone we would expect heat to be as readily convertible into work as work into heat. Since this is not the case there must be something characteristic of molecular systems to which the irreversibility is due. This "something" is discovered in the fact that heat consists of a chaotic motion of the molecules, and that as a result of collisions this motion tends to become as chaotic or disordered as possible. In other words, the irreversibility which finds expression in the second law of thermodynamics is due essentially to the fact that ordered motion always tends, of its own accord, to become disordered, and chaotic motion never tends, of its own accord, to become ordered.

This statement is a statement of the second law of thermodynamics not expressed simply as a result of experience but in terms of statistical

¹ According to Planck this assumption is "the very quintessence of the hypothesis of quanta". It must be pointed out that whilst this assumption makes the theory of quanta and Nernst's Heat Theorem agree, it is not essential to the deduction of the heat theorem itself, which only requires that the entropy of all substances at absolute zero shall be the same, but not necessarily zero.

mechanics. We have therefore found a mechanical basis for the second law.

It is obvious at the same time why Gibbs gave the significance "mixed-up-ness" to the concept of entropy; for maximum mixed-up-ness means on the mechanical view maximum stability or equilibrium, and hence when equilibrium exists the entropy is a maximum. The same idea is involved in the term "run-down-ness" employed by Tolman as a descriptive mechanical term for entropy. The latter term appeals to the mind as being particularly applicable to a chemical reaction which proceeds in order to attain an equilibrium state at which the system will, chemically speaking, have completely "run down".

THE PRINCIPLE OF EQUIPARTITION OF KINETIC ENERGY.

This principle, which has been deduced on the basis of statistical mechanics by Maxwell and by Boltzmann (*cf.* Jeans, *Dynamical Theory of Gases*), has already been employed in Chap. I. of Vol. I. in dealing with Perrin's method of determining the Avogadro Constant from measurements made upon emulsions. The principle states that in a system consisting of a large number of particles (*e.g.* molecules) the kinetic energy is on the average equally distributed amongst the various degrees of freedom possessed by these particles. The first point with which we have to deal is the term *degree of freedom*.

A degree of freedom is represented by a co-ordinate. We may take the term as meaning an independent mode in which a body may be displaced or a possible mode or direction of motion. We shall consider briefly the problem of the number of degrees of freedom possessed by bodies in the gaseous and solid states of matter respectively. First of all, a word about energy in general. We are familiar with the two kinds of energy which material systems may possess, namely, kinetic and potential. These "kinds" of energy are not to be confused with the "types" of energy of which we are about to speak. A "type" may consist of kinetic and potential energy together, or simply kinetic alone. A gas molecule can possess theoretically three *types* of energy, each of which is a function of the temperature: (1) *Energy of Translation*; (2) *Energy of Vibration*, and (3) *Energy of Rotation*.

1. *Energy of Translation*.—This type of energy is possessed in virtue of the free translational motion of the molecules along free paths throughout the whole of the system. The energy in this case is entirely kinetic. It has been represented diagrammatically in Chap. I. of Vol. I. in connection with Perrin's work on Brownian movement. Every gas molecule possesses translational motion and consequently translational energy. Since the direction of any movement of this kind can be represented by the three space co-ordinates, we conclude that translational energy corresponds to three degrees of freedom. The energy of translation is the same for any moving molecule at a given temperature. Further, such a molecule possesses just three degrees of freedom in respect of translation whether the molecule be monatomic or polyatomic;

the constitution of a molecule does not enter into the question of its translational energy.

2. *Energy of Vibration.*—This type of energy exists in virtue of the oscillations of particles with respect to a fixed centre of gravity. Vibration is only possible when there is a restoring force acting upon the particle which tends to make it take up a mean position. The existence of the restoring force is the factor which distinguishes vibration from translation and also from rotation to be mentioned later. We meet with vibration in the case of the atoms inside a molecule of a gas, in the case of electrons inside an atom, and likewise in the case of the atoms composing a solid. Vibration is always a constrained movement. We can conceive of vibration as corresponding either to one or to two or to three degrees of freedom. When we speak of vibration in connection with molecules it is always to be understood that we are referring to the vibrations of the *atoms* inside the molecule. One such atom can

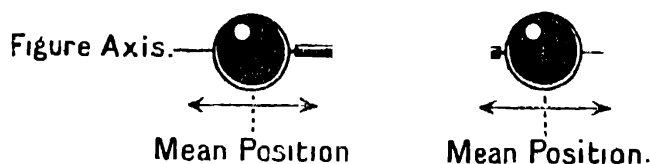


FIG. 2 (a).—*Linear vibration* of atoms in a diatomic molecule. One degree of freedom. Energy, kinetic + potential.

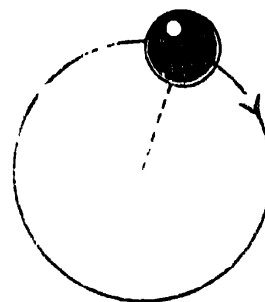


FIG. 2 (b).—*Circular vibration* of a particle round a centre of attraction. Two degrees of freedom. Energy, kinetic + potential.

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vibrate with respect to the other in the case of a diatomic molecule. In this case the vibration is linear, that is, it is along the line joining the two atom centres. Since the vibration is linear there is one degree of freedom in this case. Linear vibration is represented in diagram (a), Fig. 2.

It is also conceivable that the vibration of the particle may be circular. That is, the particle may describe a circular path about a centre of gravity, the orbit being traced out on a surface. Hence in such a case there are two degrees of freedom to be attributed to the vibration. This is represented by the mode of motion shown in diagram (b), Fig. 2. Further, in the case of a monatomic solid (such as a metal) the only type of motion which can be ascribed to the atom is vibration. Free translation cannot exist, for if it did the solid would not retain its crystalline form. In this case the vibration of every atom can take place in three directions in space with respect to the centre of gravity or mean position of the atom. There are therefore three degrees of freedom to be attributed to the vibrations.

of the ultimate particles in a solid. This is represented in diagram (c), Fig. 2. The characteristic feature of all vibrations is the existence of potential as well as kinetic energy. As will be shown later each complete vibration on the average contains just as much potential energy as it does kinetic.

To return to the vibrations of the atoms in a gas molecule. In the case of a diatomic molecule the molecule is said to possess one degree of freedom in respect of the to-and-fro vibration of one atom with respect to the other. The molecule also possesses three degrees of

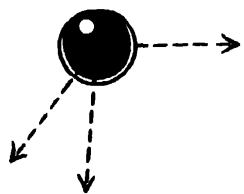


FIG. 2 (c).—Trilinear vibration of an atom in a solid. Three degrees of freedom. Energy, kinetic + potential.

freedom in respect of translation of the molecule as a whole. In a triatomic molecule the atoms ABC probably vibrate in pairs, AB, BC, CA, each pair functioning like a diatomic molecule, so that the molecule as a whole has three degrees of freedom in respect of atomic vibrations. The molecule possesses in addition three degrees of freedom in respect of translation. Hence, in the case of a triatomic molecule there are three degrees of freedom in respect of translation and three in respect of vibration.

It is obvious that no atomic *vibration* is possible in the case of a monatomic molecule in a *gas*. If such an atom is displaced there is no restoring force; the atom is not connected to any other as in the case of diatomic molecules, and any displacement would simply be identical with free translation. Contrast this with the behaviour of monatomic molecules in solids in which any displacement can only take place against a restoring force, with the result, as already mentioned, that the vibration in the case of a solid possesses three degrees of freedom. In the case of a monatomic gas vibration is impossible, and, so far as we have gone, we can only ascribe to this kind of molecule energy of the translational kind. A difficulty crops up when we come to consider a monatomic gas molecule in the light of the third possible type of motion, *viz.* molecular rotation.

3. *Energy of Molecular Rotation*.—If a molecule resembles a solid sphere we would expect it to rotate in the manner indicated in Fig. 3, diagram (a). The rotation of a sphere can be referred to three axes of rotation, *i.e.* there are three degrees of freedom. The energy is entirely kinetic. Molecules, however, are not necessarily spherical unless they contain a number of atoms. It is believed that at least three atoms must be present in a molecule before we can possibly ascribe to the molecule as a whole the limiting number (3) of degrees of freedom in respect of rotation.

It is a remarkable fact that monatomic gas molecules do not appear to possess rotational energy. This conclusion rests upon the experimental fact that the molecular heat of argon and other monatomic gases and metallic vapours can be accounted for by simply assuming *translational* energy. A monatomic gas molecule appears to function

simply as a massive point, and not as a massive sphere. This is a remarkable conclusion. It is self-evident that *vibration* of the atom cannot occur in the case of a monatomic molecule. It is by no means clear why *rotation* of the monatomic molecule as a whole apparently does not occur.

• Molecular rotations are ascribed to collisions with other molecules. This distinguishes molecular rotation from atomic vibration as far as origin is concerned. Atomic vibration can indeed be affected by collisions, but the origin of atomic vibration is more deeply seated, so to speak, than that of molecular rotations. Presumably atomic vibration is set up as a result of absorption of radiant energy on the part of the molecule. This might occur at a collision, but not necessarily so; unless the collision be very inelastic (*cf.* Chap. VII., the section dealing with resonance and ionisation potentials).

When a molecule consists of more than one atom it seems reasonable to ascribe to the *molecule as a whole* a certain amount of rotational energy. Krüger has suggested that, in place of true molecular rotations, we may have to substitute another kind of motion, namely, *precessional vibrations*.¹

The possible kinds of rotations and precessional vibrations in the case of a diatomic molecule are illustrated in Fig. 3, diagrams (b) to (e). It must be understood that rotation *or* precessional vibration always refers to the molecule as a whole. This is in contrast with the view taken of true *atomic* vibrations, which have been discussed.

As regards the rotation of a diatomic molecule the diagram (b), Fig. 3, shows us that there are two degrees of freedom, *i.e.* there are two co-ordinates at right angles defining the surface over which the rotation of such a molecule can take place. The axis of rotation is at right angles to the plane indicated in the diagram.

From the point of view of the internal molecular energy the significance of the rotation of the molecule depends upon its moment of

¹The term "precessional vibration" requires perhaps a word of explanation. The type of motion represented by the term is shown in diagrams (d) and (e), Fig. 3. It is similar to the true precession of a gyroscope, but with this difference that a diatomic gas molecule does not precess in a definite field of force. It is assumed, in fact, that there is no field of force. Precessional vibration (which must not be confused with nutation) is brought about in the case considered by the collisions of molecules with one another, each molecule being assumed to possess gyroscopic properties in virtue of the electrons which it contains, and which spin [circular vibration] around the figure axis as already indicated in diagram (b), Fig. 2. If no collision occurred a diatomic molecule would spin with a fixed axis. As a result of collision the spin is disturbed and the figure axis itself describes the circular motion represented in diagram (d), Fig. 3. It maintains this type until a further collision occurs which sets up a new vibrational precession, the figure axis now precessing round a circle which has a greater or less circumference than before. Such precessional vibrations might be more accurately described as Poincot movement, dealt with in rigid dynamics. Precessional motion has been considered here because it undoubtedly represents a *conceivable* type of mechanical motion. However, its significance for molecular properties (such as heat capacity and absorption power) is negligible, since the behaviour of molecules appears to be such as to exclude it as a really operative mode of motion (*cf.* Appendix VI.).

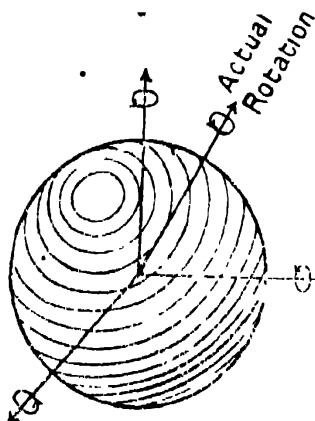


FIG. 3 (a).—Sphere with three component rotations. Three degrees of freedom. Energy, kinetic.

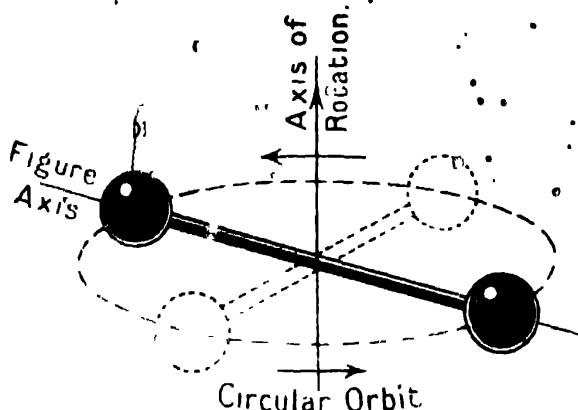


FIG. 3 (b).—Molecular rotation of diatomic molecule (due to collisions). Axis of rotation perpendicular to figure axis. Two degrees of freedom. Energy, kinetic.

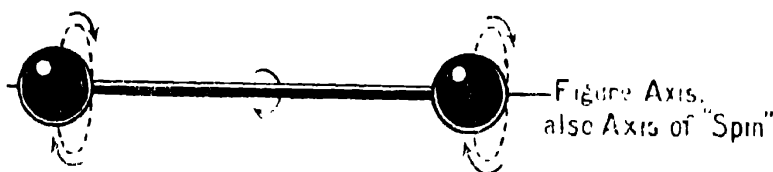


FIG. 3 (c).—Molecular rotation with axis of rotation coincident with figure axis. Two degrees of freedom. Energy, kinetic. (Motion maintained by collisions.)

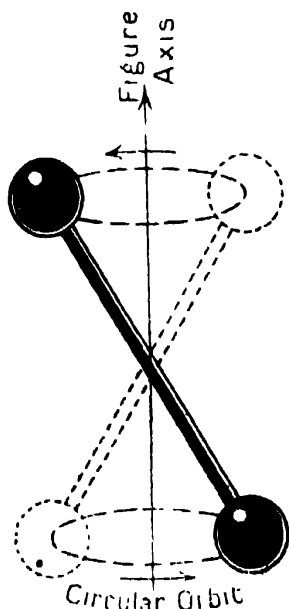


FIG. 3 (d).—Precessional vibration (due to collisions). The molecule is assumed to possess gyroscopic properties. Two degrees of freedom. Energy, kinetic.

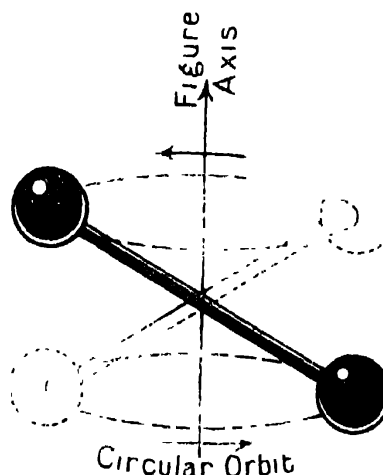


FIG. 3 (e).—Extreme precessional vibration (due to collisions at sufficiently high temperatures), merging into ordinary molecular rotation.

inertia, *i.e.* the moment of inertia of each of the atoms with respect to the axis of rotation and the number of revolutions ν which the molecule makes per second (as a result of collisions). The rotational energy is given by the expression $\frac{1}{2} I \cdot (2\pi\nu)^2$, where I is the moment of inertia and ν has already been defined.

• Fig. 3 (*c*) likewise illustrates a conceivable mode of rotation of the molecule as a whole. This case differs from Fig. 3 (*b*) in that the figure axis is coincident with the axis of rotation. As a matter of fact, although this is a conceivable mode of rotation its presence cannot be detected, say in the molecular heat of a diatomic gas. The case is very similar to the rotation of a monatomic molecule. Rotation of the type Fig. 3 (*b*), on the other hand, in which the axis of rotation is perpendicular to the figure axis is of great importance and contributes a certain amount to the observed molecular heat of a diatomic gas.

It is an important fact that, so far as the molecular heat of a gas molecule is concerned the types of motion represented by Fig. 2 (*b*), *i.e.* circular vibration of an *electron* in an atom, Fig. 3 (*c*), rotation of a diatomic molecule about the figure axis, and the rotation of a monatomic molecule, do not appear to exist, *i.e.* the conceivable degrees of freedom corresponding to such motion do not manifest themselves. At first sight this might be attributed to exceedingly small moments of inertia¹ with respect to the three kinds of motion considered, but that this cannot be a complete explanation is evident when we remember that the energy term contains not only moment of inertia but frequency of rotation as well and a small moment of inertia might be compensated by a high value for the frequency. The fact is that no satisfactory explanation of the absence of these conceivable degrees of freedom can be given on the basis of classical dynamics such as we are at present following; it is necessary to introduce certain concepts associated with the quantum theory. According to this theory, as will be seen later, the probability of any mode of motion of a rotational or vibrational kind existing depends on the magnitude of the frequency of revolution associated with the motion, the probability diminishing as the frequency increases. On the basis of the quantum theory we conclude, therefore, that molecules do not rotate in the sense of Fig. 3 (*c*)—and the same is true for the rotations of monatomic molecules—because of the extremely high frequency which would characterise such motion. The problem of the rotational energy in so far as it affects the molecular heat of gases is considered towards the end of Chap. IV.

In the case of a diatomic molecule we have therefore three degrees of freedom in respect of translation, one degree of freedom in respect of linear vibration of the atoms, and two degrees of freedom in respect of molecular rotation,—six degrees in all.

In the case of a molecule containing more than two atoms, if rotation be possible at all, it is reasonable to ascribe three degrees of

¹ The moment of inertia depends in general on the mass of the rotating particle and its distance from the centre of gravity.

freedom in respect of such rotation, *i.e.* the limiting number of degrees of freedom. At the same time the molecule possesses three degrees of freedom in respect of translation and three degrees of freedom in respect of atomic vibrations in pairs; in all nine degrees of freedom. In the case of translation and of rotation¹ the energy is entirely kinetic; in the case of vibration it is potential as well as kinetic. The possible degrees of freedom in various kinds of gas molecule are summarised in the following table which is due to Bjerrum (*Zeitsch. Elektrochem.*, **17**, 731, 1911); the general correctness of the assigned values is borne out to a certain extent by the values of the molecular heats of the respective gases:—

No. of Atoms in the Molecule.	Number of Degrees of Freedom.		
	In Virtue of Translation.	In Virtue of Rotation.	In Virtue of Vibration.
3		0	
3		2	
3		3	
3		3	

Our knowledge of the *liquid state* is so scanty that it has not been possible hitherto to assign any definite value to possible number of degrees of freedom. A liquid molecule must, of course, possess three degrees of freedom in respect of translation; it must likewise possess an unknown number in respect of rotation and vibration. We pass on, therefore, to the *solid state*. In the case of a solid, *i.e.* a crystalline substance, and probably also in the case of a super-cooled liquid like glass, it is necessary to regard translational energy (and also rotational energy) as absent, the energy possessed by the molecules of a solid being vibrational. As already stated, vibration of each atom can take place along all *three* axes, so that even the simplest type of solid possesses three degrees of freedom. We shall return to this later.

¹In regarding the rotation of a diatomic molecule as representing kinetic energy alone, we are assuming that the bond between the atoms is quite firm. In general, however, we may expect a certain amount of "give" due to the atoms being "centrifuged" from one another in the rotation. If this occurs it will involve a certain amount of potential energy. Bjerrum (*loc. cit.*) finds that the kinetic energy E_k of molecular rotation is related to the potential energy E_p by the equation—

$$E_p/E_k = RT/4\pi^2\nu^2Mr^2$$

where ν is the frequency of internal vibration, M is the mass, and r the radius of the molecule. Taking the case of oxygen at ordinary temperatures where $\nu = 10^{14}$, $r = 10^{-8}$, and $M = 32$, it is found that—

$$E_p/E_k = 0.00002.$$

That is, the potential energy of rotation is negligible compared with the kinetic energy.

For the present we have to take up the application of the principle of equipartition of (kinetic) energy amongst degrees of freedom. According to this principle, when a system is in *statistical equilibrium*, such equilibrium being determined by a number of variables, *i.e.*, degrees of freedom, to each such variable *one must attribute the same quantity of (kinetic) energy*. It is to be remembered that there is no restriction as regards the physical state of the system—the principle applies equally well to gaseous, liquid, or solid systems and to systems embracing two or more such states simultaneously. It is supposed to hold equally well also for degrees of freedom in respect of translation, vibration, or rotation. To see how much this energy amounts to per degree of freedom, let us consider the kinetic energy of translation of a perfect gas at a given temperature. First of all we have the relation—

$$PV = RT.$$

Further, we have seen in the theoretical deduction of Boyle's Law that—

$$P = \frac{1}{3}\rho u^2$$

where ρ is the density of the gas and u the root-mean-square velocity. If we are considering 1 gram-molecule of the gas, $\rho = \frac{\text{molecular weight (M)}}{V}$ where V is the molecular volume, and hence we can write—

$$PV = \frac{1}{3}Mu^2 = \frac{1}{3}Nmu^2$$

where m is the mass of a single molecule and N the number of molecules in 1 gram-mole. Taking into consideration the first equation, we obtain—

$$RT = \frac{1}{3}Mu^2 = \frac{1}{3}Nmu^2.$$

Now the kinetic energy of a single molecule is $\frac{1}{2}mu^2$, and hence the kinetic energy of 1 gram-mole is $\frac{1}{2}Nmu^2$. That is the kinetic energy of 1 gram-mole is $\frac{3}{2}RT$, and this holds good whether the gas be monatomic or polyatomic. Now a gas molecule has three degrees of freedom in virtue of translation, and hence by applying the equipartition principle, EACH DEGREE OF FREEDOM POSSESSES KINETIC ENERGY EQUAL TO $\frac{1}{2}RT$.

This is the quantitative form of the principle of equipartition of energy between degrees of freedom. The principle does not mean that in a gas system, for example, the kinetic energy of translation of every molecule shall be exactly $\frac{3}{2}kT$, where k is the gas constant per single molecule. We know from Maxwell's distribution law that the kinetic energy varies in general from molecule to molecule. What the equipartition principle does mean is that on the average the kinetic energy of a molecule is $\frac{3}{2}kT$.

Let us now consider the special case of a monatomic gas. As we have

already seen, it can possess no vibrational energy: whether it possesses rotational energy is at this stage a doubtful point. Its energy, due to translational motion, for 1 gram-mole at T° abs. is $\frac{3}{2}RT$, when $R = 1.985$ cal. Now the specific heat C_v at constant volume is simply the increase in the *total* energy per degree. If we are dealing with 1 gram-mole or gram atom as unit of mass, the heat term will be the so-called molecular or atomic heat C_v . It is clear from definition that the increase in the

(kinetic) energy of translation¹ per 1° rise in temperature $= \frac{\partial}{\partial T}(\frac{3}{2}RT) = \frac{3}{2}R = 2.98$ cal. per mole. Experiments of Pier in Nernst's laboratory (*Zeitsch. Elektrochem.*, **15**, 546, 1909; **16**, 897, 1910) have shown that the molecular heat of argon is 2.98 cal. per mole, and further that this is *independent* of temperature. This agreement suggests that one should neglect the rotational energy of the monatomic molecule (vibration of atoms inside the molecule is naturally impossible since the gas is monatomic).² In fact the monatomic molecule seems to function as a massive point. Agreement of this order between calculated and experimental values is, however, not found in other cases. Thus, taking the case of a *diatomic* gas, the number of degrees of freedom in virtue of translation is again 3. The number of degrees of freedom in virtue of vibration we have considered as 1; that is 4 degrees in virtue of translation and vibration. The corresponding kinetic energy of such a molecule will be $4 \times \frac{1}{2}RT = 4.0 T$ cal./mole, if the law of equipartition be assumed. Of course this does not represent all the energy due to translation and vibration. In vibrations we have potential energy as well as kinetic which must be taken account of. It can be shown by a simple calculation that the potential energy of a particle undergoing what we might call "circular vibration" (cf. fig. 2(b))³ is just *equal* to the kinetic energy of the vibration. The calculation is as follows:—

Consider a particle whose mass is m travelling in a circle round a centre of gravity with velocity u . Suppose r is the radius of the circular path. A motion of this kind involves the action of two opposing forces, one tending to draw the particle towards the centre, its position of rest, the other due to the motion of the particle tending to make it fly off at a tangent. The two forces must just balance in order to make the circular movement permanent. Let us suppose that the diameter of the circle, *i.e.* the amplitude of the vibration, to be so small that the force tending to draw the particle back to the centre is proportional to the distance of the particle from the centre. This very simple law of attraction can only hold when the particle is not far removed from the centre, *i.e.* when r is small. If A is this attractive force per unit dis-

¹ Energy of translation is necessarily entirely kinetic, and it is to the distribution of *kinetic* energy amongst degrees of freedom that the law of equipartition is properly to be applied.

² The monatomic gas is again considered from the point of view of the quantum theory, in Chap. IV., in connection with the "molecular heat of hydrogen at low temperatures."

distance from the centre, then, on the assumption just made, the force acting inwards at a distance r is Ar . We have now to calculate this force in terms of the motion of the particle. Consider the particle traversing the circular path shown in the figure (Fig. 4).

Suppose that the particle is at the point a , travelling with a velocity u in the direction aT . After a short interval of time δt it is at b travelling with a velocity u in the direction bT . The arc $ab = u\delta t$, and so the radian measure of the angle aob or cd is $\delta\theta = u\delta t/r$. If $TC = TD = u$, then the velocity has changed from one represented in magnitude and direction by TC to one represented by TD . By the triangle of velocities, the change in velocity is represented in magnitude and direction by the line cd . The direction of cd is the same as that of TO ; and its magnitude is $2u \sin \delta\theta/2$. In the limit when δt is infinitesimally small $\sin \delta\theta/2 = \delta\theta/2$, or the change of velocity is $u\delta\theta$, i.e. $u^2\delta t/r$.

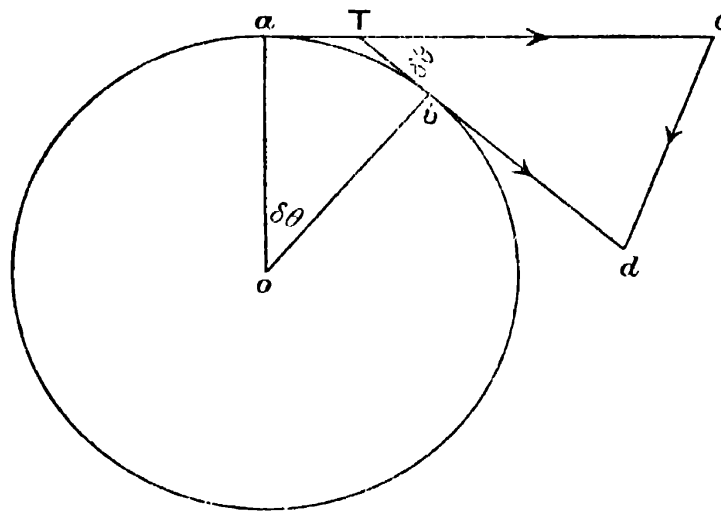


FIG. 4.

Hence the acceleration inward (viz. the velocity inward divided by δt) is equal to u^2/r . But force = mass $\times$ acceleration. Hence the force acting inwards and preventing the particle from flying off is mu^2/r . This must be identical with Ar . That is—

$$mu^2/r = Ar.$$

Further, the potential energy of the particle at a (namely, the work which must be done upon the particle to bring it from the position of rest, the centre of the circle, to the point a on the circumference) is the product of the force acting into the distance traversed. The force varies at every stage of the radius, so that it is necessary to integrate the work expression for each increment dr in order to obtain an expression for the potential energy of the particle at the point a . That is, the potential energy of the particle when it is on the circumference is $\int_0^r Ar dr$ which

is $\frac{Ar^2}{2}$. But it has just been shown that $Ar = mu^2/r$. Hence the potential energy, viz. $\frac{Ar^2}{2}$ is equal to $(1/2)mu^2$. But the term $(1/2)mu^2$ is the average kinetic energy of the particle. Hence in a complete circular vibration the kinetic energy is just equal in magnitude to the potential energy.

We return now to the question of the diatomic molecule.

The linear vibration executed by one atom with respect to the other involves one degree of freedom, i.e. the line of junction of the two atoms. On the equipartition principle the kinetic energy involved per mole is $\frac{1}{2}RT$. Since there is likewise an equal amount of potential energy, the total energy due to vibration is $1RT$. Adding the amount due to the (kinetic) energy of translation of the diatomic molecule as a whole, viz. $\frac{3}{2}RT$, we obtain $\frac{5}{2}RT$ as the total energy due to translation and vibration. That is, the rise in this energy per 1° is $\frac{5}{2}R = 5.0$ cal. per mole per degree, taking $R = 2$ cal. If now we take rotation of the molecule as a whole into account we again have two degrees of freedom, to which one must assign RT units of kinetic energy. The total energy of a diatomic molecule, provided the law of equipartition is true, and *provided ALL the degrees of freedom are effective*, should be $\frac{7}{2}RT$, and the molecular heat therefore $\frac{7}{2}R = 7.0$ approx.

Experiment shows, however, very different values. For hydrogen at 0°C . the molecular heat $C_v = 4.9$ to 5.2 cal. per degree, and at 2000°C ., $C_v = 6.5$ cal. (cf. Nernst, *Zeitsch. Elektrochem.*, **17**, 272, 1911). For nitrogen at 0°C ., $C_v = 4.84$, and at 2000°C ., $C_v = 6.7$. For chlorine at 0°C ., $C_v = 5.85$, at 1200°C ., $C_v = 7.0$. For oxygen at 0°C ., $C_v = 4.9$, at 2000°C ., $C_v = 6.7$. These values are only approximately correct. It is evident, however, that not only is there lack of agreement in the numerical values between those observed and those calculated at lower temperatures, but the fact that the *molecular heat of diatomic gases varies considerably with the temperature is quite unaccounted for by the theory of equipartition* unless, indeed, the number of degrees of freedom is a function of the temperature; which is difficult to believe.

In the case of triatomic gas molecules the degrees of freedom in respect of translation are three, the [kinetic] energy corresponding being $\frac{3}{2}RT$. As regards vibration, there are possibly three vibrating pairs, each with one degree of freedom, corresponding to the quantity $3 \times \frac{1}{2}RT$ of kinetic energy. To this has to be added an equivalent amount of potential energy, making $3RT$ as the total energy term in respect of vibration. Hence translation and vibration apparently entail $\frac{9}{2}RT$ units of energy, and the increase in this for 1° rise in temperature is $\frac{9}{2}R = 9.0$ cal. per mole per degree. Logically we should likewise add a term for rotation of the molecule as a whole, which we have seen amounts to $\frac{3}{2}RT$. The observed molecular heat C_v for CO_2 at 18° is 7.09 , and this becomes 10.47 at 2210° (Pier, *l.c.*). For water vapour C_v at 50°C . = 5.96 (Nernst and Levy), and at 2327°C ., $C_v = 9.68$ (Pier). Again, the discordance between theory and experiment is very

apparent since theory predicts a *constant* molecular heat of either 9 or 12 cal. per mole per degree.

The Ratio γ for Gases, and the Number of "effective" Degrees of Freedom.

It may easily be shown (cf. Meyer's *Kinetic Theory of Gases*, p. 140 seq.) that the ratio $\frac{C_p}{C_v}$ or γ can be expressed approximately in the form—

$$\gamma = 1 + \frac{2}{n}$$

where n is the number of degrees of freedom of the gas molecule. In the case of monatomic gases the value of γ is 1.666, and this is the quantity which is obtained on putting $n = 3$ in the above expression. That is, a monatomic gas molecule possesses three degrees of freedom, in respect of translation only. This agrees with the conclusion we came to above (though, of course, it must be remembered that the actual number of degrees is *possibly* greater than this, i.e. degrees in virtue of rotation, but for some unknown reason only some are effective in regard to heat capacity, for after all an atom is *not* a point in the mathematical sense). In the case of a diatomic molecule the value of γ , found by experiment, is in many cases 1.4, and this will correspond to putting $n = 5$ in the above equation. In triatomic gas molecules $\gamma = 1.3$ in general, and this makes $n = 7$. These numbers are certainly less than the actual number of degrees of freedom possessed by di- and triatomic gases, as is indeed shown by the fact that there are some diatomic gases with as small a value as 1.29 for γ (iodine vapour) and some triatomic gases, e.g. CS_2 , for which $\gamma = 1.2$. *Further, the values of γ are not constant but vary with the temperature.* The whole problem of the number of degrees of freedom is, therefore, in a very unfinished state.

The doubt which exists, in the case of polyatomic molecules, regarding the true number of degrees of freedom, takes away from the force of the criticism levelled against the principle of the equipartition, on the ground of the lack of agreement between observed and calculated molecular heats. The soundest criticism of the principle rests on the experimental observation that the molecular heat *varies* with the temperature, whilst the principle leads us to expect it to be constant, no matter how many degrees of freedom be present.

Atomic Heat of Solids.

Since the equipartition principle is considered to hold equally well for all states of matter, the term $\frac{1}{2}RT$ must represent the *kinetic* energy per degree of freedom of 1 gram-mole of any system at the temperature T . In solid elements—the metals—it is generally agreed that the gram-molecule and gram-atom are identical, so that in such a case $\frac{1}{2}RT$ is the kinetic energy per degree of freedom for each gram-atom,

R being put equal to 1.935 cal. The orientation of the atom of a metal is such, that it is free to vibrate in any direction which can be resolved in terms of the three space co-ordinates X, Y, Z. Such a particle possesses three degrees of freedom¹ (cf. Fig. 2, diagram (d)).

The kinetic energy in virtue of this "space" vibration is evidently $\frac{3}{2}RT$, and since any vibration² involves an amount of potential energy equivalent to the kinetic, the total energy of 1 gram-atom of a monatomic solid is $3RT$, according to the principle of equipartition of energy. Now the atomic heat C_v at constant volume is simply the change of total atomic energy per degree, that is—

$$C_v = \frac{d}{dT}(3RT) = 3R = 5.955 \text{ cal.}$$

The application of the equipartition principle has therefore led to the conclusion that the atomic heat of monatomic solids should be a constant, viz. 5.955, the same for all monatomic solids and independent of temperature (the term $3R$ does not contain T ; though, of course, the total energy present in the solid at any given temperature depends on this temperature, viz. $3RT$ in the above case). This result is practically identical with Dulong and Petit's experimentally discovered law, and this agreement is one of the most striking pieces of evidence in favour of the equipartition principle. The following table gives the values of atomic heats for a number of elements at 20° C. (cf. G. N. Lewis, *Journ. Amer. Chem. Soc.*, **29**, 1168, 1907):—

$$3R = 5.955.$$

Element.	Atomic Heat at Constant Volume	Element.	Atomic Heat at Constant Volume.
Na	6.4	Cd	5.9
Mg	5.8	Sn	6.1
Al	5.6	Sb	5.9
K	6.5	I	6.0
Fe	5.9	Pt	5.9
Ni	5.9	Au	5.9
Cu	5.6	Tl	6.1
Zn	5.7	Pb	5.9
Pd	5.9	Bi	6.2
Ag	5.8		

The approximation of these values to that of $3R$ is obviously very close. Nevertheless, too great stress cannot be laid upon this, for *it has been shown by experiment that the atomic heat of solids (as in the case of gases) is a function of the temperature, decreasing to very small values at*

¹ In the case of metals each atom vibrates independently of others, at least as long as its amplitude is less than the mean distance of the atoms apart, and hence three degrees of freedom must be ascribed to it.

² That is, any vibration of the simple harmonic kind, in which the restoring force is proportional to the distance from the centre.

very low temperatures. We shall take this question up later on in discussing the work of Einstein and Nernst. Sufficient has been said, however, in this connection to show that while the principle of equipartition is *partially* true, in the form given by Boltzmann it is not sufficiently comprehensive. It might be thought that a sufficient explanation of the observed increase in atomic heat with rise in temperature lies in the supposition of new degrees of freedom coming into existence. We cannot, however, imagine a "fractional" degree of freedom. It must either exist definitely, or not at all. One would expect therefore, that the atomic heat should rise by *steps* as the temperature rises. All observations, however, have shown that the increase in atomic heat is a perfectly *continuous* function of the temperature. Leaving the problem of specific or atomic heats, let us turn to another important problem, namely that of thermal radiation; for it was through investigation carried out in this field that the modifications of the principle of equipartition were eventually introduced, which in the hands of Planck and Einstein have permitted a satisfactory explanation to be given of the discrepancies hitherto existing between theory and experiment, not only in the domain of radiation itself, but likewise in that of the heat content of solids. Whether these modified views form the ultimate solution of the problem, it is at present impossible to say. They represent, at any rate, a fundamental stage in the development of the subject.

APPLICATION OF [CLASSICAL] STATISTICAL MECHANICS TO RADIATION.

The fundamental problem in radiation is: how is the energy, which is radiated, distributed amongst the various wave-lengths which may be regarded as constituting the radiation?

We are here concerned with temperature radiation only. A definition of this term has already been given, together with a short account of the radiation laws in Chap. XIV. of Vol. II.

In studying the question of radiation, that is of the exchange of radiant energy between matter and ether, it is necessary, of course, to limit our consideration to the equilibrium state. If an enclosed material system is maintained at a temperature T , the interior of the system contains energy constantly radiated to and from the boundary. When these energy exchanges arrive at equilibrium each cubic centimetre of the system contains energy in what we may call the undulatory form. The problem is how to calculate the *most probable* distribution of the energy between the various wave-lengths, not only for the single temperature T but for any temperature; for the equilibrium state may be defined as that for which the distribution of energy (at the given temperature) between the various wave-lengths is the most probable. To work out this statistical problem we must know something about the number of degrees of freedom possessed by the matter and by the ether (present throughout the matter) respectively. It will now be shown that absolutely different results are arrived at, according as to whether

we regard the ether as continuous (*i.e.* structureless) or regard it as having a structure. Let us first consider the ether as continuous. In this case the ether is a medium capable of vibrating in an *infinite* number of ways, the wave-lengths propagated throughout it having all possible values between 0 and ∞ . This is the same thing as saying that the ether possesses an *infinite* number of degrees of freedom. Matter imbedded in the ether has, on the other hand, a *finite* number of degrees of freedom in virtue of its discontinuity, *i.e.* in virtue of its discrete or heterogeneous structure. If now we apply the principle of equipartition of energy to such a system composed of both matter and ether, it is clear that the ether will take all the energy (since its number of freedoms is infinite) leaving none at all for the matter.

The following mechanical analogy is suggested by Jeans. Let us suppose that we have a number of corks held together by elastic and floated upon the surface of still water. Cause the corks to move violently to and fro. Waves will be formed, *i.e.* energy will be given out from the cork system to the water by this kind of "radiation," as well as by friction, until finally the corks come to rest. All the energy originally given to the corks has now passed to the water. Permanent movement of the corks is unthinkable. It will be observed that the cause of this lies in the fact that the corks are large units compared with water molecules; in fact, the water is a sensibly continuous medium compared with the coarse-grained structure consisting of corks. It is impossible therefore to conceive of an equilibrium being set up as regards energy interchange between matter and ether except at the absolute zero of temperature. In other words, we cannot deduce any radiation law. It is clear, therefore, we must follow out some other line of reasoning. Let us take the second case, namely, the assumption that the ether does possess a structure. On this basis the number of degrees of freedom of the ether is no longer infinite, and it is possible to conceive of equilibrium states being reached at different temperatures as a result of energy transfer between matter and ether. If we think of the ether as possessing a fine-grained structure, it follows that the waves which can be propagated by such a medium must not become shorter than a certain limiting size λ_0 . It is easy to see this by analogy. Waves which can be transmitted by a material system (sound waves, for example) must be great compared with the distance of the molecules which compose the system, as otherwise the waves would not be transmitted at all. Similarly, we must suppose that even the shortest light waves which we know of must be large compared with the grain structure of the ether itself. If this structure exists it ceases to be legitimate to speak of infinitely short waves in the mathematical sense. The shortest conceivable waves must be of the order of magnitude of the distance apart of the "molecules of the ether".

Starting out with the idea that the number of degrees of freedom possessed by the ether is finite, Jeans has shown that by applying the principle of equipartition of energy, the energy distributes itself in the normal spectrum in such a way that the intensity—corresponding to a

region lying between λ and $\lambda + d\lambda$ —is proportional to the temperature and inversely proportional to the fourth power of the wave-length. That is, the energy in the spectrum will so distribute itself that it will be almost entirely confined to the region of extremely short wave-lengths. As a matter of fact, however, this is not the real distribution of energy in the spectrum. It has been shown experimentally that the intensity of energy radiating from a black body and in equilibrium with the body shows a maximum for waves in the infra-red region at ordinary temperatures, and vanishes almost completely for very long or very short waves. Representing it graphically we obtain a curve containing a maximum, as already shown in Fig. 53, Vol. II. On the other hand, the theoretical expression for the distribution of radiation energy, referred to above (which expression is identical with Rayleigh's radiation law, already stated in Chap. XIV., Vol. II., *viz.* $8\pi kT\lambda^{-4} \cdot d\lambda$), yields a curve which contains no maximum but rises rapidly as the wave-length diminishes.¹

We are considering the case in which wave-lengths of all magnitudes exist between the infinitely long denoted by the symbol λ_{∞} and the limiting value λ_0 , but none shorter than this. If we integrate the Rayleigh-Jeans expression between the limits λ_0 and λ_{∞} , we obviously obtain an expression for the total radiant energy in the enclosure. The integration leads to the expression—

$$\frac{8}{3} \frac{kT}{\lambda_0^3}$$

It follows from this expression that only one-eighth of the total energy will be of wave-length greater than $2\lambda_0$, whilst seven-eighths reside in wave-lengths between $2\lambda_0$ and λ_0 itself. In the case of the ether—if we give it a structure at all—the size of its grain cannot be greater than 10^{-8} cm. (the order of magnitude of a gas molecule). Taking this value, however, as applying to the ether structure, it follows that no wave-length shorter than 10^{-8} cm. can be transmitted. (As a matter of fact we know that X-rays are about this order of magnitude.) Even with this limit to the wave-length it can be shown on the basis of the Rayleigh-Jeans formula that only one-millionth of the total energy would reside in wave-lengths of the order 10^{-6} cm. and longer. This is quite contrary to what is observed, for the greater part of the energy is known to lie in the region 10^{-4} to 10^{-3} cm. We conclude, therefore, that the assumption that the number of degrees of freedom of the ether is not infinite, is in itself insufficient to yield an expression (involving the equipartition principle) which will agree with experiment. We are forced to the conclusion, therefore, that the principle of equipartition itself is not applicable to the problem of distribution of radiant energy between matter and the ether. The result obtained on the equipartition basis always gives a partition of energy of such a kind that the energy is almost entirely confined to the short wave-lengths, and in the limit, *i.e.* if the

¹ A deduction of the Rayleigh-Jeans formula is given in Appendix II.

ether be structureless, the energy goes completely into the ether and no distribution is possible at all. Experiment shows, on the other hand, that distribution certainly does exist, and furthermore, the distribution does not require that all the energy shall be located in the shortest wave-lengths; on the contrary, the distribution is such that very little energy is distributed among the very short or the very long waves, the greater part of it belonging to waves of intermediate magnitude. This is indicated by the maximum in the intensity curve obtained in measurements of the amount of energy radiated from a heated body.

In the foregoing we have considered a number of problems, atomic heats of solids, molecular heats of gases, and radiation phenomena, from the point of view of classical statistical mechanics as expressed in the principle of equipartition of energy between degrees of freedom. In each case we find that the conclusions arrived at on this basis hold over a limited region, but fail to give a complete explanation of the phenomena observed. It is obvious that some additional hypothesis must be introduced, or rather, we must be prepared to discard the principle of *equipartition* and substitute for it some other kind of partition law. An attempt to do this has been made by Planck in his quantum hypothesis, which will be discussed in the following chapter.

CHAPTER II.

Planck's concept of quanta—Planck's radiation formula.

THE fundamental modification introduced by Planck consists in discarding the principle of *equipartition* of kinetic energy. The equipartition principle assumes interchange of energy in a continuous manner, *i.e.* without any lower limit to the amount of energy transferable. Planck assumes, on the other hand, that the exchanges of energy between matter and ether, instead of taking place in any proportion whatsoever, can only take place by steps, that is, in multiples of some small energy unit, the energy unit itself being a function of the vibration frequency concerned. We might regard radiant energy itself as possessing a structure. Planck himself regards the matter from a different standpoint. It would be more correct to say that the definite concept of radiant energy itself being discrete in nature is that upheld by Einstein, a view which has been given a clearer physical basis by J. J. Thomson, who considers a radiant-energy unit or "quantum" as a region of periodic disturbance travelling along a Faraday tube. In place of a continuous ether, we have therefore to substitute a number of stretched strings of ether, each string being a Faraday tube differentiated in some (practically unknown) way from the "space" surrounding it. This statement is, however, to be taken rather as a rough material analogy than as an exact description or formulation, for any exact description is at the present time impossible. Planck, on the other hand, lays stress not on the question of the ultimate structure of radiant energy itself so much as on the *mode* of its absorption and emission by matter. The energy radiated by one element of a black body is partially absorbed by other elements. Each one of the vibrators, or "resonators," as Planck calls them, which constitute the material element in question, can only emit (and absorb) energy in certain fractions. (This at any rate is Planck's first position; we shall see later that he has modified the above view.) A word here about the Planck resonators. It was pointed out in the chapter on photochemistry in Vol. II. that the vibrating particles which produced visible and ultra-violet light were much smaller than the atoms of the substance and were therefore in all probability the electrons. The amount of energy contributed to the "total" spectrum by the visible or ultra-violet region has been shown by experiment (*cf.* Lummer and Pringsheim's curve, Fig. 53, Vol. II.) to be a very small fraction of the

whole (even at fairly high temperatures). The main part of the energy is confined to the infra-red region. These long waves are considered as emitted and absorbed by the *atoms* of the substance being set in vibration. These statements apply only to the continuous spectrum given out by a black body in the first instance and in general by heated metals. Planck's resonators for the infra-red may therefore be identified with the atoms (electrically charged); for the ultra-violet, with the electrons. But Planck in the theoretical treatment of the subject has regarded his resonators as *linear*, that is, he only considers the energy caused by vibration in a single direction. Such a vibration entails one degree of freedom. If we were to apply the equipartition principle to a system of such linear resonators, we would ascribe to each resonator RT units of energy made up of $\frac{1}{2}RT$ kinetic energy and an equivalent quantity of potential. It is only for extremely long waves that the equipartition principle holds (as is shown by the degree of applicability of Lord Rayleigh's formula for radiation), and that only for a limited temperature range. *The essence of Planck's view is that it discards the equipartition principle.* It will be noted that the linear resonators of Planck are considered to possess only one-third of the total vibrational energy of the actual atoms (of a solid), each of which possesses three degrees of freedom—as already pointed out in connection with the values for atomic heat.

According to Planck, the material resonators considered do not react with, or are not influenced by, *infinitely* small quantities of radiation energy, using the word infinitely in its strict sense. Planck's hypothesis may be stated thus: *A resonator is only capable of absorbing or emitting a certain finite amount of energy of magnitude ϵ .* (As already mentioned, Planck later modified this statement by supposing absorption to be continuous, but emission discontinuous, *i.e.* in quanta.) It will be clear how this hypothesis modifies the principle of equipartition of energy among various degrees of freedom. To any degree of freedom which actually possesses energy we cannot ascribe less than one quantum (ϵ), and the actual quantity possessed will be an integral multiple of one quantum. With this distribution of energy some of the degrees of freedom may possess no energy at all, *i.e.* the *equipartition* idea breaks down.

The term "the quantum" requires now to be considered. Although we speak of this as the unit of (radiant) energy, it must be clearly understood that *it is NOT a fixed and constant quantity of energy.* According to Planck, the quantum, ϵ , *i.e.* its size or magnitude, is a function of the vibration frequency (either of the radiation, supposing this to be monochromatic, or what amounts to the same thing, the frequency of the resonator). In fact, according to Planck, there is direct proportionality between the magnitude of ϵ and the frequency ν , this proportionality being expressed in Planck's fundamental relation—

$$\epsilon = h\nu$$

where h is a universal constant (Planck's constant) having the numerical value 6.5×10^{-27} erg-seconds.¹

Now the *smaller* the unit the *greater* the probability that a resonator will possess at least one or some quanta. If we consider a material system, made up of molecules, atoms, and electrons, such a system possesses resonators of various dimensions, *i.e.* capable of vibrating with different frequencies. Such a system can absorb or emit a range (or spectrum) of vibration frequencies. Considering the very short waves, *i.e.* large vibration frequency, the quantum ϵ corresponding to this is large, and hence the chance that a resonator possesses even one quantum of this size is less than in the case of longer waves, where each quantum is a smaller magnitude. Less energy of the short wave type will therefore be emitted than that of the longer wave type. That is, the energy of the radiation emission curve falls off in the short wave region. In this way Planck explains the observed diminution in energy emitted in the visible and ultra-violet region, as shown in Lummer and Pringsheim's curves. Further, in the region of extremely long waves ν is relatively very small, and hence the size of the unit ϵ is small, so that for extremely long waves the actual energy contribution made by this region will be small. We should therefore expect, on Planck's view, the energy wave-length curve to pass through a maximum, as is actually the case.

Starting out with Planck's hypothesis of the discrete nature of absorption and emission of radiation, it is now necessary to see what radiation formula may be deduced; in other words, what theoretical expression can be deduced for the distribution of energy in the spectrum of a body emitting temperature- (*i.e.* black-body-)radiation. For an exact and complete account, the reader is referred to Planck's *Theory of Heat Radiation*. We can only here attempt an abbreviated and approximate deduction, based upon a method employed by Jeans (*Phil. Mag.*, 20, 953, 1910).

If a vibration—that is, a very small spectral region lying between λ and $\lambda + d\lambda$, which corresponds experimentally to monochromatic radiation—can possess the following amounts of energy, *viz.* 0, ϵ , 2ϵ , . . . etc., then the ratio of the probabilities of these events, as in the usual gas theory calculations, is—

$$1 : e^{-\epsilon/kT} : e^{-2\epsilon/kT} : \text{etc.}$$

where e is the base of natural logarithms, k a constant, namely, the gas constant per molecule, and T the absolute temperature. This means that if we represent by "1" the number of vibrations possessing no energy at all, then the number of vibrations, each of which possesses one unit of magnitude ϵ , will be $e^{-\epsilon/kT}$, and so on. Instead of thinking of vibrations in "space," let us think of the resonators or vibrations of

¹ Planck (*Annalen der Physik*, [4], 4, 553, 1901) has shown that the magnitude of ϵ is a function of ν by applying Wein's displacement law to an expression obtained by him for the entropy of a system. The reader should also consult Planck's *Theory of Heat Radiation*, 2nd edition.

matter which can emit or absorb such vibrations. Let us suppose that the material system consists of a great number of similar vibrators (emitting and absorbing the wave-length λ), each acting independently, then if we represent by unity the number of such resonators which possess no energy, the term $e^{-\epsilon/kT}$ gives the number of resonators possessing ϵ units each, etc. If out of N such resonators under consideration M have zero energy, the number of resonators, each of which has energy ϵ , is $Me^{-\epsilon/kT}$, the number having energy 2ϵ is $Me^{-2\epsilon/kT}$, and so on. Hence, for the total—

$$\begin{aligned} N &= M + Me^{-\epsilon/kT} + Me^{-2\epsilon/kT} + Me^{-3\epsilon/kT} + \text{etc.} \\ &= M(1 + e^{-\epsilon/kT} + e^{-2\epsilon/kT} + \text{etc.}) \\ &= \frac{M}{(1 - e^{-\epsilon/kT})} \end{aligned}$$

And if ΣU is the total energy of the N resonators—

$$\begin{aligned} \Sigma U &= M \times 0 + \epsilon \times Me^{-\epsilon/kT} + 2\epsilon \times Me^{-2\epsilon/kT} + \text{etc.} \\ &= \frac{M\epsilon e^{-\epsilon/kT}}{(1 - e^{-\epsilon/kT})^2} \end{aligned}$$

Substituting the value for N already given, we obtain—

$$\Sigma U = \frac{N\epsilon}{e^{\epsilon/kT} - 1}.$$

If we now substitute $h\nu$ for ϵ , we obtain—

$$\Sigma U = \frac{Nh\nu}{e^{h\nu/kT} - 1}.$$

And for the energy of one such resonator we obtain the *mean* value—

$$U = \frac{h\nu}{e^{h\nu/kT} - 1}.$$

The same expression may be obtained in a different manner (*cf.* Appendix II.).

So much for the energy of a single vibrating resonator in radiation equilibrium with its surroundings, the expression being based on the hypothesis that energy is made up of units, the magnitude of a unit being directly proportional to the vibration frequency of the resonator. We have now to see the connection between this term U and the radiation density u_ν , that is, the quantity of monochromatic radiation (frequency ν) energy per c.c. of radiated space. Although u_ν is usually referred to as the radiation density, *i.e.* energy per unit volume, the term u_ν itself has not got the dimensions of energy/volume. The correct expression for radiation density is $u_\nu d\nu$, where $d\nu$ represents a narrow strip of the spectrum virtually monochromatic. In using the symbol u_ν for radiation density the quantity $d\nu$ is implied. Physically a single

• wave-length 'has' no meaning ; we always work with a very narrow strip of spectrum containing the wave-length or frequency denoted by λ or ν . [In actual practice a heated body does not give out monochromatic radiation, but a complete spectrum. We shall define u_ν in different terms later, though still equivalent to the above.]

• Planck has shown on the basis of the classical electro-magnetic theory (which therefore introduces no unitary hypothesis) that u_ν and $\bar{U}$ are connected by the relation—

$$\bar{U} = \frac{c^3}{8\pi\nu^2} \cdot u_\nu \quad \dots \quad (1)$$

[Cf. Planck, *Annalen der Physik*, [4], 4, 560, 1901; Lindemann, *Brit. Ass. Rep.*, 1912. If we take $\lambda = 800\mu\mu$ as a mean value for a wave-length in the red part of the spectrum, it is easily calculated from this formula that $U = 8u$ (approx.). Similarly for the violet end of the spectrum, taking $\lambda = 400\mu\mu$, one finds $U = 2u$ (approx.).]

By combining the two expressions obtained above, the mean value of the density of energy radiated from a single resonator in a system consisting of a large number of similar resonators, all emitting monochromatic light of frequency ν (*i.e.* between the limits ν and $\nu + d\nu$), is given by the expression—

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} \cdot d\nu.$$

This is one of the forms of Planck's Radiation Formula.

We wish now to change the shape of this expression a little, in order to be clear about the relation of the term u_ν and the term E_λ , which latter we have already met with in Wien's radiation formula (*cf.* Chap. XIV., Vol. II.).

The total energy (say in ergs) radiated per second from unit area of a black body emitting a continuous spectrum covering the wave-lengths 0 to ∞ has been denoted by S . This is the term which appears in Stefan's Law, *viz.* $S = \sigma T^4$, the temperature of the source being T and the radiation purely "temperature" radiation. Now S is the quantity of energy which would be present in an imaginary cylinder, 1 square centimetre base and length 3×10^{10} cms. (since 3×10^{10} cms. is the distance which the radiation will travel in one second). The cylinder is supposed to be placed with its base on the radiating body and extending out into space. The volume of this cylinder is 3×10^{10} c.c., and since this contains S ergs of energy the space density of the radiation,

i.e. the amount of energy per c.c. is $\frac{S}{3 \times 10^{10}}$ erg. Denoting the space

density of the energy by E , we have $E = \frac{S}{3 \times 10^{10}}$ or $S = 3 \times 10^{10} E$, the term E referring, of course, to the entire range of wave-lengths

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between 0 and ∞ emitted by the body. This total density E may be expressed thus—

$$E = \int_{\lambda=0}^{\lambda=\infty} \frac{\partial E}{\partial \lambda} \cdot d\lambda.$$

Let us write $E_\lambda = \frac{dE}{d\lambda}$, then $E = \int_0^\infty E_\lambda d\lambda$.

It will thus be seen that E_λ is a *rate* (the rate of change of E with λ). We might also define it as the *density* of the energy radiated from a spectral region the wave-length limits of which differ by unity. This, though correct, is physically inconceivable. It would entail the existence of a spectrum the wave-length limits of which differ by 1 cm., a difference enormous compared to any actual limits reached. It is therefore much less confusing to think of E_λ as being the small energy-density increment ΔE divided by the correspondingly small spectral width $\Delta \lambda$ (or more accurately $\frac{\partial E}{\partial \lambda}$ as above). The expression $E_\lambda d\lambda$ or $\frac{\partial E}{\partial \lambda} d\lambda$ is therefore the energy-density of the radiation between λ and $\lambda + d\lambda$. Planck gives an analogous significance to the term $u_\nu d\nu$. Thus the energy-density of the total spectrum may be written—

$$E = \int_{\nu=0}^{\nu=\infty} \frac{\partial E}{\partial \nu} d\nu$$

or writing $u_\nu = \frac{\partial E}{\partial \nu}$, $E = \int_0^\infty u_\nu d\nu$.

The term u_ν is also a rate, or it may be defined as the density of the energy radiated from a spectral region, the limits of the vibration frequency differing by unity. Numerically u_ν is of quite a different order of magnitude from E_λ . Thus, since $\lambda = \frac{c}{\nu}$, where c is the velocity of light, it is evident that $\frac{d\lambda}{d\nu} = -\frac{c}{\nu^2}$, so that on increasing ν by unity (*i.e.* corresponding to the production of $u_\nu \times 1$ energy-density units) the wave-length decreases by the amount $\frac{c}{\nu^2}$. This gives a result of the order 10^{-18} in the case in which the infra-red wave-length region $\lambda = 1\mu$ is considered. Since E_λ is the energy-density corresponding to a wave-length difference of *unity*, the term E_λ is $10^{16} u_\nu$ for the region in which the vibration frequency differs by unity.

The shortest wave-length physically possible, *i.e.* the shortest wave-length capable of being emitted or absorbed by an atomic-electronic mechanism (such as that associated with a molecule), is of the order of magnitude of very hard X-rays, namely, 10^{-9} cm. This sets a limit, therefore, to the width of spectrum which can be regarded as possessing a physical meaning. It is interesting to see what this limiting width is when expressed in terms of the difference of the frequencies between

the "edges" of the strip. Let us suppose that the strip is chosen in the middle of the visible spectrum. The mean value of λ is then 0.6μ or 6×10^{-5} cm., the limiting value to be ascribed to $d\lambda$ being 10^{-9} cm. The frequency difference $d\nu$ which corresponds to $d\lambda$ is given by—

$$d\nu = -\frac{c}{\lambda^2} \cdot d\lambda.$$

That is, for the case considered,

$$= d\nu = \frac{3 \times 10^{10} \times 10^{-9}}{36 \times 10^7} = 10^1$$

Hence, in the region of the spectrum referred to, the smallest width to which we can attach a physical meaning corresponds to a frequency difference of the order 10^{10} . The actual or absolute frequency in the middle of this strip is of the order 5×10^{14} .

In bolometric or spectro-photometric determinations we measure the energy ΔS radiated per second by a small region or strip of a continuous spectrum which lies between λ and $\lambda + \Delta\lambda$. Since $S = 3 \times 10^{10} E$, and therefore $\Delta S = 3 \times 10^{10} \Delta E$, we can calculate $\frac{\Delta E}{\Delta\lambda}$ which in turn is identical with E_λ . We now wish to express the radiation formula of Planck in such a way as to allow of convenient comparison between E_λ observed and its value as given by the formula. To do this let us rewrite the formula already given:—

$$u_\nu d\nu = \left(\frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} \right) d\nu.$$

Remembering that $u_\nu d\nu = E_\lambda d\lambda$, and further that $d\lambda = -\frac{c}{\nu^2} d\nu$, we obtain directly—

$$E_\lambda = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{ch/\lambda kT} - 1} \quad (2)$$

which is the more usual form of Planck's equation for the distribution of energy throughout the spectrum. As already pointed out, we can compare the observed and calculated values of E_λ for a whole series of small regions and thus test the equation over the complete spectrum. It has been found that the above formula reproduces the actual energy distribution from a black body in an extremely accurate manner, being in fact the most satisfactory equation yet proposed. The principal experimental investigations are those of Lummer and Pringsheim (*Verh. d. Deutsch. physik. Gesell.*, **1**, 23 and 215, 1899; **2**, 163, 1900), Rubens and Kurlbaum (*Sitzungsber. d. K. Akad. d. Wissenschaft zu Berlin*, **41**, 929, 1900; *Annalen d. Physik*, [4], **4**, 649, 1901), Paschen (*Annalen d. Physik*, [4], **4**, 277, 1901), and the more recent measurements of W. Coblentz (*Bull. Bur. Standards*, 1914, **10**, p. 1). Cf. also Appendix III.

By way of illustration a few of Paschen's results may be quoted.

The extent of the spectrum examined was from $\bar{\nu}$ to 8.8μ (*i.e.* the infra-red region), measurements being carried out by means of the bolometer. Using a fluorite prism (which is more transparent than quartz) successive parts of the spectrum could be isolated. The radiating body consisted of a hollow vessel or cylinder, electrically heated to any desired temperature, the cylinder being either of platinum or porcelain with or without a coating of copper oxide. In the following table i denotes the magnitude of the swing of the galvanometer needle, a certain swing corresponding to a certain amount of energy communicated by the radiation to the bolometer. After calibrating the apparatus, Planck's formula can be used to calculate values of i for different wave regions, and these may be compared with experiment.

TABLE I.— $\lambda = 1.0959 \mu$. Width of spectrum isolated = $3'$.
Temperature of surroundings = 9.8°C .

T Temperature of Radiator		1553.1.	1325.3.	1038.7	
i	Observed	60.6	252.6	59.3	3.65
	Calculated from Wien's equation	61.14	252.5	59.14	3.61
	Calculated from Planck's equation	61.27	249.4	58.97	3.68

TABLE II.— $\lambda = 8.7958 \mu$. Width of spectrum isolated = $6'$.
Temperature of surroundings = 15.1°C .

Temperature of Radiator	1458.6.	1069.8	844.4.	625.6	483.1.
i { Observed	131.7	74.43	41.51	20.46	9.22
Wien's equation . . .	90.40	59.79	39.52	19.86	9.08
Planck's equation . .	129.1	73.75	44.83	20.90	9.22

It will be observed that Planck's formula is much more applicable than Wien's for high temperatures and long waves. Besides the infra-red region, the experiments of Paschen and Wanner, as well as those of Lummer and Pringsheim, on radiation from the visible spectral region, have shown that Planck's formula holds here also within the limits of experimental error. In addition to the direct method of testing Planck's formula outlined above, its validity is further shown by the fact that we can deduce from it directly the Rayleigh-Jeans law, *viz.*, $E_\lambda = 8\pi kT/\lambda^4$ which holds for large values of λT , Wien's law which holds for small values of λT , the displacement law (*viz.* $\lambda_{\text{max.}} \times T = \text{constant}$, and $E_{\text{max.}} = \text{constant} \times T^5$), and the Stefan-Boltzmann law for total radiation. The deductions are as follows. Writing the Planck radiation formula in the form—

$$E_\lambda = \frac{8\pi ch}{\lambda^5} \cdot \frac{e^{h/\lambda kT}}{e^{h/\lambda kT} - 1} \quad (2)$$

- It will be observed that for small values of λT (i.e. small compared with ch/k) equation (2) becomes :—

$$E_{\lambda} = \frac{8\pi ch}{\lambda^5} \cdot e^{-ch/\lambda kT}$$

which is Wien's law of energy distribution.

On the other hand, for large values of λT the term $e^{ch/\lambda kT}$ in (2) is small and may be expanded in the form, $1 + ch/\lambda kT$, whence,

$$E_{\lambda} = \frac{8\pi ch}{\lambda^5} \cdot \frac{\lambda kT}{ch} = \frac{8\pi kT}{\lambda^4},$$

which is the Rayleigh-Jeans equation of energy distribution. As already pointed out in the preceding chapter, the Rayleigh-Jeans law is based on classical statistical mechanics and does not involve the concept of quanta. In agreement with this it will be observed that if h becomes vanishingly small this condition leads to the same conclusion already arrived at when λT was small, viz. equation (2) becomes identical with the Rayleigh-Jeans expression.

The Stefan-Boltzmann expression for total radiation is obtained as follows (cf. Planck, *Heat Radiation*, p. 171) :—

For the space density u of all types of thermal radiation in a vacuum at a temperature T we have :—

$$u = \int_0^{\infty} u_{\nu} d\nu$$

and since

$$u_{\nu} d\nu = \frac{8\pi h \nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} \cdot d\nu$$

it follows that

$$u = \frac{8\pi h}{c^3} \int_0^{\infty} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}$$

$$u = \frac{8\pi h}{c^3} \int_0^{\infty} \left(e^{-h\nu/kT} + e^{-2h\nu/kT} + e^{-3h\nu/kT} + \dots \right) \nu^3 d\nu$$

and integrating term by term,

$$u = \frac{48\pi h}{c^3} \cdot \left(\frac{kT}{h} \right)^4 \cdot \alpha = \frac{48\pi k^4}{c^3} \cdot \alpha \cdot T^4,$$

where α stands for the series : $1 + \frac{1}{2^4} + \frac{1}{3^4} + \dots = 1.0823$.

It is thus seen that the space density of total radiation (which is directly proportional to the amount of energy of all wave-lengths radiated from a black body per second at temperature T) is proportional to T^4 as the Stefan-Boltzmann law requires. The symbol u is identical with E already employed in this chapter.

We have next to show that Planck's equation leads to the displacement law of Wien.

Denoting by $\lambda_{\max}$, the wave-length at which the thermal radiation emitted from a uniformly heated enclosure attains a maximum it follows that:—

$$\left(\frac{dE_{\lambda}}{d\lambda} \right)_{\lambda=\lambda_{\max}} = 0.$$

On differentiating Planck's equation (2) with respect to λ , substituting the value $\lambda_{\max}$, and equating to zero, we obtain:—

$$e^{-\frac{ch}{kT\lambda_{\max}}} + \frac{ch}{5kT\lambda_{\max}} - 1 = 0$$

whence

$$ch/kT\lambda_{\max} = 4.9651$$

or

$$\lambda_{\max} \times T = ch/4.9651k = \text{a constant}$$

as is required by the displacement law.

Further, writing down equation (2) and allowing for the fact that at the position at which the E is a maximum the wave-length multiplied by the temperature is a constant, b say, we have:—

$$E_{\max} = \frac{8\pi ch T^5}{15} \cdot \frac{1}{e^{\frac{ch}{kbT}} - 1} = \text{const.} \times T^5.$$

Planck's expression is thus a very comprehensive one.¹ From it may be deduced all the observed relations characteristic of radiation from a black body or full radiator.

We have now to employ certain experimental values obtained in radiation measurements in order to calculate the values of the two

¹ To emphasise further the fact that Planck's formula is at variance with the principle of equipartition of energy among various degrees of freedom, it is interesting to calculate the energy of an electron vibrating with a frequency identical with that of the ultra-violet region when light is emitted, and compare this energy with the energy of an atom or of a gaseous molecule possessing the mean kinetic energy characteristic of ordinary temperature (say 300° absolute), (cf. J. Stark, *Zeitsch. physik. Chem.*, 86, 53, 1913). The frequency ν for the ultra-violet region will be about 5×10^{14} per second. Planck's expression for the mean energy of a single resonator is, as we have already seen—

$$\bar{U} = \frac{h\nu}{e^{h\nu/kT} - 1}.$$

For ordinary (low) temperatures— $T = 300^\circ$ —this expression reduces to $\bar{U} = h\nu e^{-\frac{h\nu}{kT}}$, since ν is large and T small. The mean energy of an electron resonator is therefore $\bar{U}$, where $\bar{U} = 1 \times 10^{-16}$ ergs. The mean kinetic energy of a gas molecule at the ordinary temperature $= \frac{3}{2}kT = 6 \times 10^{-14}$ ergs, so that instead of equipartition of energy we find that the energy of the electron vibrating in the atom or molecule is only one five-hundredth part of the mean kinetic energy of translation of the molecule itself. This argument, it will be observed, is based on the Planck Oscillator. • We shall see later however that the actual motion of an electron in an atom is very different from that envisaged here. Cf. the atomic model of Bohr (Chap. V).

Fundamental constants h and k . The latter is the gas constant reckoned for a single molecule and not for the gram-molecule. It is evident that the accuracy with which h and k can be calculated depends on the accuracy of the radiation measurements themselves. In Appendix 3 a number of values are collected, based on a critical examination by Coblentz of the best existing data. For the present purpose it is sufficient to indicate the method of calculation of the constants, employing the experimental data of individual investigators. The more exact value of h based on the average of a considerable number of measurements is appended.

Kurlbaum (*Wied. Ann.*, **65**, 759, 1898) has found by experiment that the total energy emitted from 1 square centimetre of a "black body" in 1 second, the temperature of the body being 100°C. and that of the air being taken as 0°C. , amounts to $0.0731 \text{ watt/cm.}^2$, that is—

$$S = S_{100^\circ \text{C.}} - S_{0^\circ \text{C.}} = 4.2 \times 7.31 \times 10^5 \text{ ergs/cm.}^2\text{-sec.}$$

By applying Stefan's law we obtain—

$$S = \sigma(373^4 - 273^4).$$

$$\text{Hence } \sigma = \frac{4.2 \times 7.31 \times 10^5}{(373^4 - 273^4)} \frac{\text{ergs}}{\text{cm.}^2\text{-sec.-degrees}^4}$$

The physical significance of σ is evidently the total radiation emitted from a black body per second, when the temperature difference between the black body and the surroundings is 1 degree, the temperature of the black body being 1° absolute, the surroundings being at 0° absolute. Corresponding to this emission at 1° absolute, we see that E or u , i.e. the total energy density, is $\frac{\sigma}{\times 10^{10}}$, that is—

$$E_{1^\circ \text{abs.}} = \frac{4.2 \times 7.31 \times 10^5}{3 \times 10^{10}(373^4 - 273^4)} = 7.061 \times 10^{-15} \frac{\text{ergs}}{\text{c.c.}}$$

Now $E = \int_0^\infty E_\lambda d\lambda$, or $\int_0^\infty u_\nu d\nu$ and E_λ or u_ν is given by Planck's expression. We have already obtained a value for u or E so that we can write (remembering that $T = 1$)—

$$E_{1^\circ \text{abs.}} = \frac{48\pi k^4}{c^3 h^3} \times 1.0823.$$

Setting this equal to the "observed" value of $E_{1^\circ \text{abs.}}$ viz. 7.061×10^{-15} , we obtain—

$$\frac{k^4}{h^3} = 1.1682 \times 10^{15} \quad \dots \quad (3)$$

Further, Lummer and Pringsheim (*Verh. d. Deutsch. physik. Gesell.*, **2**, 176, 1900) have determined the value of $\lambda_{\text{max.}} T$, where $\lambda_{\text{max.}}$ is the wave-length corresponding to the maximum value of E_λ from a black

body radiating at a given temperature. The expression $\lambda_{\max.} \times T$ is a constant independent of temperature, as Wien has shown, the numerical value found by Lummer and Pringsheim being 0.294 cm. degrees. We have already seen, on the basis of Planck's formula, that—

$$\lambda_{\max.} \times T = \frac{ch}{4.9651k}$$

or

$$\frac{h}{k} = \frac{4.9651 \times 0.294}{3 \times 10^{10}} = 4.866 \times 10^{-11} \quad (4)$$

By combining equations (3) and (4) we obtain finally—

$$h = 6.55 \times 10^{-27} \text{ erg/sec.}$$

$$k = 1.346 \times 10^{-16} \text{ erg/degree.}$$

Millikan (*Proc. Nat. Acad. Sci.*, **3**, 314 (1917)) gives as the most accurate value of the charge e on an electron, the quantity $4.774 \pm 0.005 \times 10^{-10}$ electrostatic units. Knowing this quantity and the value of e/m , *viz.* 1.767×10^7 , and also knowing Rydberg's constant for the Balmer series in the hydrogen spectrum,¹ *viz.* 3.290×10^{15} according to Millikan, the value of Planck's constant h may be calculated with a high degree of precision. The value given by Millikan is—

$$h = 6.547 \pm 0.011 \times 10^{-27}$$

which is in close agreement with that “observed” by Millikan (6.56) and by Webster (6.53). More recently, Birge (*Physical Rev.*, **14**, 361, 1919) gives as the most exact value—

$$h = (6.5543 \pm 0.0025) \times 10^{-27}.$$

The Significance of the Constant k, and a Determination of the Number of Molecules in one gram-molecule.

Consider once more the Planck expression for the energy of vibration of a large number of similar resonating particles emitting monochromatic radiation, *viz.*—

$$\Sigma U = \frac{N\epsilon}{e^{\epsilon/kT} - 1}.$$

The expression $e^{\epsilon/kT} - 1$ may be expanded thus—

$$\frac{\epsilon}{kT} + \frac{1}{2} \left(\frac{\epsilon}{kT} \right)^2 + \text{higher powers.}$$

If now we are dealing with a system vibrating at very high tempera-

¹ Cf. Bohr's theory of the atom (Chap. V.), according to which Rydberg's constant = $\frac{2\pi^2 e^4 m}{h^3}$.

ture it will be seen that the above expression becomes $\frac{\epsilon}{kT}$. That is, at high temperatures—

$$\Sigma \bar{U} = \frac{N\epsilon}{\frac{\epsilon}{kT}} = NkT.$$

Exactly the same result is obtained at less high temperatures if the system is vibrating very slowly, for in this case ν is small (relatively), and since $\epsilon = h\nu$ the quantity ϵ is likewise small. In both cases the quantity ϵ vanishes from the expression for the sum of the energies of the vibrating particles, this energy being simply proportional to the absolute temperature. Under these conditions we reobtain the results of the ordinary kinetic theory, *i.e.* the principle of equipartition of energy, it being no longer necessary to consider the energy as other than continuous. The principle of equipartition of energy is therefore true as a limiting case for large values of T and for small values of ν . Suppose that we are dealing with a solid radiating energy at a temperature sufficiently high that the energy of vibration of the resonators could be represented by NkT . The resonators, as employed by Planck, are linear, *i.e.* they possess 1 degree of freedom, to which one would ascribe (if the equipartition principle applied, *i.e.* if T is sufficiently high) $\frac{1}{2}RT$ kinetic and $\frac{1}{2}RT$ potential, in all RT units of energy per gram-mole or gram-atom, if a monatomic solid be considered, and if the atoms be identified with the resonators.¹

Hence, the term ΣU reckoned for N "linear" atoms where N is now regarded as the number of atoms in a gram-atom (or molecules in a gram-mole) should be identical with RT . That is, $RT = kNT$, or $R = kN$. The constant k is therefore simply the gas constant reckoned for a single molecule.

This may be tested at once by calculating N from the known value R (per mole), and from the value of k calculated from radiation data, using Planck's formula. In this way it is found that $N = 6.175 \times 10^{23}$, a number which agrees very well indeed with the values obtained by Perrin and Millikan (*cf.* Vol. I., Chap. I.). This "radiation" method may therefore be regarded as a new and independent method of calculating the Avogadro constant. The value of N just given leads to a value for the charge on an electron, *viz.* 4.69×10^{-10} electrostatic units, which agrees well with Millikan's value, 4.774×10^{-10} .²

¹ The actual atoms in solids vibrate with three degrees of freedom. For the present we are considering "linear" atoms or atoms possessing 1 degree of freedom.

² In the above calculation the value of k was obtained from radiation data. The most accurate, because the most direct, method of obtaining k is simply to divide R by N .

According to Millikan the most accurate value for N is 6.062×10^{23} .

Hence $k = \frac{R}{N} = \frac{83.2 \times 10^6}{6.062 \times 10^{23}} = 1.37 \times 10^{-16} \text{ ergs/degree.}$

Numerical Values of the Size of the Quantum ϵ in different Spectral Regions.

In the following table are collected some values of $(h\nu)$ extending over a wide range. The longest wave measured by Rubens, in 1910, was $\lambda = 90\mu$, though still longer waves have been measured more recently. The shortest wave-length quoted is 0.1μ , or $100\mu\mu$ (Schumann).

Wave-length λ .	$= h\nu$		
$\lambda = 90\mu$.	3.3	10^{11}	2.1×10^{-1} ergs
$\lambda = 6\mu$.	5	10^{11}	3.3×10^{-1}
$\lambda = 2\mu$. (This is the region of maximum intensity when the body is at 1646° absolute)	1.5		9.9×10^{-1}
$\lambda = 0.8\mu$. (This is approximately the limit of the visible red)	3.75		2.47×10^{-1}
$\lambda = 0.4\mu$. (This is approximately the limit of the visible violet)	7.5		4.95×10^{-1}
$\lambda = 0.2\mu$. (This is the limit obtainable with a quartz prism)	1.5		9.9×10^{-1}
$\lambda = 0.1\mu$. Schumann rays	3.0		1.9×10^{-1}

Over the region referred to the value of ϵ thus varies from 10^{-11} to 10^{-14} ergs, according to the vibration frequency of the resonator, *i.e.* the vibration frequency of the radiation. As already pointed out, the resonators emitting short waves are probably electrons, those emitting long waves are probably the atoms. As regards the total energy emitted from a heated body, we can neglect the portion due to wave-lengths shorter than 0.8μ , *i.e.* we can neglect the visible and ultra-violet regions. This is true, of course, only for bodies the temperature of which is not higher than 1600° C. If the temperature of the radiator be raised much higher than this, the contribution from the visible may no longer be negligible, since in accordance with Wien's displacement law the position of maximum energy emission shifts towards the shorter wave region the higher the temperature. A body with the temperature of the sun (say 6000° C.), radiating purely thermally (without chemical effects in addition, as is the case with the sun), would have its maximum emission of energy at $\lambda = 0.5\mu$ approximately, *i.e.* in the blue-green region. It is of course quite impossible to realise a temperature so high as this under any experimental conditions.

In connection with Einstein's view of the quantum hypothesis, namely the view that radiation itself consists of small units travelling through space, it is necessary to point out one important phenomenon which it is very difficult to reconcile with this view. The phenomenon is that of interference of light, when two beams starting in the same phase have traversed paths which differ in length. The difficulty of

expecting interference on the Einstein view is very considerable, especially when it is recalled that interference can be produced—as in certain experiments of Michelson—with a difference of path of 40 cms., a distance which is enormously great compared with one wave-length.

PLANCK'S SECOND QUANTUM HYPOTHESIS.

Planck's Modified Equation for the Energy of an Oscillator.

(Cf. Planck, *Ber. d. Deut. physik. Gesell.*, **13**, 138, 1911.)

The essential modification here introduced is that while emission of radiant energy takes place in quanta, and therefore discontinuously, absorption can take place continuously. Planck was led to consider this as more probable than the older view, one important reason having to do with the question of time. Supposing absorption took place in quanta only, then an oscillator might be exposed to radiation so weak as not to yield even one quantum, under which condition the oscillator would absorb no energy at all. This would be especially true for large values of ν (large units). Further, even in those cases in which absorption could occur, it is conceivable that in weak radiation there might be a time interval.

On the former view the energy U of an individual oscillator could be expressed by $U = n\epsilon$, where n is an integer. If absorption is continuous, the total energy can no longer be regarded as an exact multiple of ϵ , but could in general be regarded as consisting of $n\epsilon$ units plus a quantity ρ over. That is—

$$U = n\epsilon + \rho.$$

Now the limits for the value of ρ are zero and one ϵ . If we are considering a large number of oscillators ρ will have an average value $\frac{\epsilon}{2}$ or $\frac{h\nu}{2}$, so that we can write for an individual oscillator—

$$U = n\epsilon + \frac{h\nu}{2}.$$

On the older view Planck's equation for $\bar{U}$, i.e. the *mean* energy to be ascribed to one oscillator in a system containing many, is—

$$\bar{U} = \frac{h\nu}{e^{h\nu/kT} - 1},$$

The new expression for $\bar{U}$ can therefore be written—

$$\bar{U} = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} = \frac{h\nu}{2} \left(\frac{2}{e^{h\nu/kT} - 1} + 1 \right)$$

or
$$\bar{U} = \frac{h\nu}{2} \left(\frac{e^{h\nu/kT} + 1}{e^{h\nu/kT} - 1} \right).$$

Planck points out several consequences of this new expression.

When $T = 0$, $\bar{U}$ is not $= 0$, but $= \frac{h\nu}{2}$. This "residual energy," remains with the oscillator even at 0° absolute. It cannot lose it since it cannot emit anything less than *one* $h\nu$. "At high temperatures and for long waves in the region where the Jeans-Rayleigh Law holds, the new formula passes into the old."

For short waves (visible and ultra-violet region) $e^{h\nu/kT}$ becomes large compared with unity, and we have—

$$\bar{U} = \frac{h\nu}{2}.$$

As regards the question of the specific heats of solids considered in the following chapter, it is pointed out by Planck that measurements of specific heat cannot be used to compare the older and newer forms of $\bar{U}$ since C_v is $d\bar{U}/dT$, and differentiation removes the additional term $\frac{h\nu}{2}$. Planck doubts whether the new expression can be tested experimentally by any direct means.¹

In the case of actual matter we naturally look for the oscillators to be associated in some way with the ultimate particles which constitute matter. The oscillators may be electrons or atomic nuclei or parts of the latter. The discontinuity assumed in the emission process has been pictured by Sir Joseph Larmor (*Phil. Mag.*, **42**, 592 (1921)) by making use of the analogy of a clock in which the periodic movement of the pendulum is maintained for a relatively long period of time (that is, for a period during which the oscillations of the pendulum are numerous and regular) by the energy of a coiled spring acting through the escapement. If the pendulum were left to itself it would rapidly slow down to rest. The function of the escapement arrangement in a clock is to give discontinuously a certain small amount or quantum of energy to the pendulum to keep it going without disturbing its regularity of motion. On the Rutherford-Bohr view of the atom which is discussed in Chap. V. an atom is supposed to consist of a nucleus surrounded by a number of electrons, the latter determining the chemical properties of the atom as well as the spectral emission. On Larmor's analogy the coiled spring is identified with energy associated with the nucleus which is transferred by something analogous to an escapement to the outer electrons which thus function as the pendulum. "A connection between the feed of energy and the free period $\epsilon = h\nu$ is, however, wanting. Perhaps also the clock may be reversible and by absorbing incident radiant energy of proper periods into its pendular system may wind up its spring—pointing ultimately to instability and ejection of a particle from the core in the manner recognised."

¹ Planck refers to a paper by Stark (*Phys. Zeitsch.*, **9**, 767 (1908)), on the application of the quantum theory to canal rays. As regards an attempt to distinguish between the old and new form of the quantum theory, see A. Einstein and O. Stern (*Annalen der Physik*, [4], **40**, 551, 1913). Cf. also Chap. IX. of this Vol., section dealing with heat of reaction.

PLANCK'S THIRD QUANTUM HYPOTHESIS.

(Cf. Planck, "An Altered Formulation of the Quantum Hypothesis," *Sitzungsber. Preuss. Akad.*, 1914, p. 918).

The assumptions employed by Planck in this modified form of the Quantum Theory are as follows:—

1. The exchange of energy between the resonators and the radiation is regarded as continuous for emission and absorption equally. This replaces the second formulation according to which emission is discontinuous, absorption continuous. The new assumption means that the interchange of energy between oscillators and radiation is governed by classical electrodynamics, so that, for example, the mean energy $\bar{U}$ of an oscillator is related to the energy density of radiation by the expression—

$$u_{\nu} = \frac{8\pi\nu^2}{c^3} \bar{U}.$$

2. The exchange of energy between resonators and free particles (molecules, ions and electrons) occurs in terms of quanta. In the collision of a free particle with a resonator it is assumed that the latter gives up to the particle the *whole* of the (vibrational) energy which it happens to possess at the moment, whilst the particle imparts to the resonator the largest amount of its own kinetic energy which can be represented by a whole multiple of the quantum $h\nu$, ν being characteristic of the resonator. In the case of solids it is assumed that there are a few vapour molecules present which function as the intermediaries and exchange energy in terms of quanta with the resonators. At the same time the number of such vapour molecules is regarded as being too small to affect sensibly the specific heat of the solid.

The view is more logical than the Second Hypothesis. The main difficulty is to conceive of a physical interpretation of an oscillator.

Planck's radiation law has been deduced by Einstein by a method which does not require any detailed information regarding the mechanism of the interaction between resonators and radiation. This is given in Chap. V., section entitled: "Einstein's use of a generalised Bohr model to deduce the radiation law of Planck."

Up to this point the most important experimental evidence which we have considered in support of the quantum theory is the fact that Planck's radiation formula quantitatively reproduces experimental values over the entire range of the spectrum investigated. In the next chapter we shall deal with further experimental evidence in connection with the atomic heats of solids which likewise is strongly in favour of the concept of quanta.

CHAPTER III.

(Physical equilibrium in solids)—Theory of atomic heats of solids—Equations of Einstein, Nernst-Lindemann, and Debye.

Einstein's Extension of Planck's Quantum Theory to the Calculation of Specific Heats of Solids (Crystalline Substances) and Supercooled Liquids ("Amorphous Solids"). (Cf. Einstein, *Annalen der Physik*, [4], **22**, 180, 1907.)

THE specific heat of a substance at constant volume is defined as the increase in total energy when the substance rises 1° in temperature. Let us take as our unit of mass the gram-mole or gram-atom (in the case of monatomic substances), and we then can write—

$$C_v = \frac{dU}{dT}.$$

NOTE.—U here stands for total energy possessed by the substance at a given temperature. It is not to be confused with the significance attached to U in the "elementary thermodynamical treatment" (Chap. I., Vol. II.), in which "U" stood for *decrease* in total energy due to chemical reaction.

Let us now restrict our attention to solids (or supercooled liquids), taking as particular instances the metallic elements. These, as we have seen, are regarded as monatomic, so that the gram-atom and gram-molecule are identical terms in these cases. Now we want to find out to what the total or internal energy of a metal is due. It is usual to regard the solid state as characterised by vibrations of the atoms about their respective centres of gravity. Such vibrations can, of course, take place in the three dimensions of space, *i.e.* each atom possesses three degrees of freedom. As we have seen, each vibration represents energy, one-half of which is kinetic, one-half potential, as long as the amplitude of the vibration is not too great. This vibrational energy is regarded as representing all the internal energy possessed by the atom, at least at low temperatures (at high temperatures the energy of vibration of the electrons inside each atom would have to be considered, but at ordinary temperature and at lower temperatures the total energy of the solid may be ascribed to the vibration of the atoms). We have already discussed this, and we have seen that on applying the principle of equipartition of energy the atomic heat of metals should be $3R = 5.955$ cal. per degree, and that this should be independent of temperature. As already pointed out, this numerical value is certainly

approximated to at ordinary temperatures, but instead of being independent of temperature, it varies, becoming continuously smaller as the temperature is lowered. The question therefore which arises is how this variation with temperature is to be accounted for. Einstein in 1907 made the first successful attempt at the solution of this problem by suggesting that Planck's quantum theory—which Planck himself had applied with so much success to the problem of the emission of radiant energy—could also be applied to the vibrational energy of the atoms, *i.e.* to the total internal energy of the solid, the temperature coefficient of which is identical with the specific or atomic heat of the substance in question: Planck's expression for the average energy of vibration of a linear resonator (*i.e.* an atom vibrating along *one* of the dimensions of space) is, as we have seen—

$$U = \frac{h\nu}{e^{h\nu/kT} - 1}.$$

[It will be observed that we are employing Planck's earlier hypothesis.] The energy of vibration of an atom capable of vibrating along the three dimensions of space will be three times this quantity, and if we denote this average vibrational energy per gram-atom by U , we get—

$$U = \frac{3N h\nu}{e^{h\nu/kT} - 1}.$$

The significance of U is identical with that which has been ascribed to it in Chap. II., Vol. II., namely, the total energy per mole or gram-atom. In the case considered one-half of U is kinetic, one-half potential energy. N denotes the number of atoms in one gram-atom. On Planck's earlier view the vibrational energy possessed by each atom must be an even multiple of one quantum. On the "classical" view ("structureless energy," so to speak) we should say that all possible differences in energy content would manifest themselves in a system made up of a large number of vibrating particles. On applying the unitary theory of energy we must recognise that a number of atoms have no vibrational energy at all, *i.e.* are at rest. Of those vibrating the energy content cannot fall below the quantum ϵ , where ϵ is three times Planck's quantum ϵ . We have, therefore, sets of atoms containing energy of the following amounts:—

0, ϵ , 2ϵ , 3ϵ , and so on.

In order to bring the expression for U given above into the form used by Einstein, Nernst, and others, we shall make a slight change in the symbols. If we denote the ratio of Planck's two fundamental constants k and h by β_0 ¹ we can write $\frac{h}{k} = \beta_0 = 4.87 \times 10^{-11}$ C.G.S. units.

Also, since $k = \frac{R}{N}$, where $R = 1.985$ calories, we can write $h\nu = \frac{R}{N}\beta_0\nu$.

¹ This is frequently written as β . The slight change is here introduced to prevent any confusion with β , one of the terms in Nernst's "heat theorem" equations of A and U .

The expression for U then becomes—

$$U = 3R \cdot \frac{\beta_0 \nu}{e^{\beta_0 \nu / T} - 1}$$

It will be observed that this equation differs from the expression $3RT$ (obtained by applying the *equipartition* principle, energy being regarded as continuous), by the substitution of the term $\frac{\beta_0 \nu}{e^{\beta_0 \nu / T} - 1}$ in place of T .

Differentiating U with respect to T we obtain Einstein's equation for the atomic (or molecular) heat of a solid at constant volume, *viz.*—

$$C_v = \frac{dU}{dT} = 3R \cdot \frac{e^{\beta_0 \nu / T} \cdot \left(\frac{\beta_0 \nu}{T} \right)}{(e^{\beta_0 \nu / T} - 1)^2}$$

On the “classical” view, the factor multiplied by $3R$ would have been unity. The “correction” term will be seen to contain T and is there-

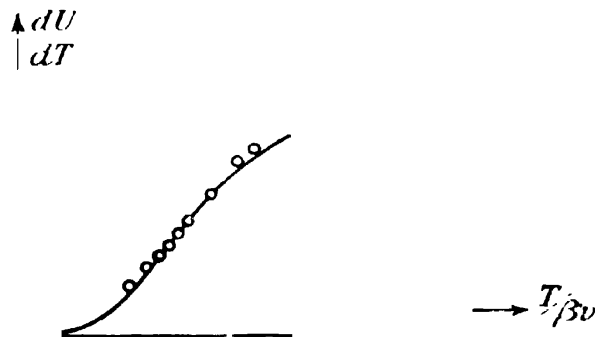


FIG. 5.

fore a function of temperature. On Einstein's theory one would expect the atomic heat itself to be a function of temperature, as is experimentally the case. Qualitatively, therefore, this marks a considerable advance over the older theory. It still remains to be seen whether the expression given really reproduces the values of C_v at various temperatures quantitatively. The shape of the curve for $\frac{dU}{dT}$ as given by Einstein's formula is shown in the accompanying figure (Fig. 5), in which the ordinates represent atomic heats and the abscissæ the temperature expressed in terms of $\frac{T}{\beta_0 \nu}$. For any given substance the vibration frequency is taken to be a constant.

It will be seen from the figure that when $\frac{T}{\beta_0 \nu} > 0.9$ the term $\frac{e^{\beta_0 \nu / T} \cdot \left(\frac{\beta_0 \nu}{T} \right)}{(e^{\beta_0 \nu / T} - 1)^2}$ approximates to unity, so that the atomic heat becomes

equal to $3R$. Dulong and Petit's Law is, therefore, a consequence of Einstein's theory when the temperature is not too low. This region of temperature is evidently reached at room temperature in the case of the majority of metallic elements. As in radiation phenomena we see that the equipartition principle applied in the ordinary way yields results (in connection with atomic heat) which are in agreement with experiment when the temperature reaches a certain magnitude. Einstein tested his equation not on the data available in the case of a metal but on the diamond. Some of the results are given in the subjoined table. They are also indicated by circles in the figure. Einstein chose the experimentally determined value for C_p at $T = 331.3^\circ$ and hence calculated ν , using the value so obtained to calculate the values of C_p at other temperatures. The experimental data (quoted) refer, as a matter of fact, to C_p , *i.e.* the atomic heat at constant pressure. In the case of the diamond—though not so in other cases—the difference between C_p and C_v is small. In the following section we shall consider the question of the independent determination of ν and C_p respectively.

ATOMIC HEAT OF CARBON (DIAMOND).

T (absolute),	$T/\beta_0 \nu$.	C_v calculated from Einstein's equation.	C_p observed (Weber).
222.4	0.1679	0.762	0.76
262.4	0.1980	1.146	1.14
283.7	0.2141	1.354	1.35
306.4	0.2312	1.582	1.58
331.3	0.2500	1.838	1.84
358.5	0.2705	2.118	2.12
413.0	0.3117	2.661	2.66
479.0	0.3615	3.280	3.28
520.0	0.3924	3.631	3.63
879.7	0.6038	5.290	5.29
1079.7	0.8147	5.387	5.39
1258.0	0.9403	5.507	5.51

Measurements of C_p of the diamond at low temperatures down to 30° abs. have been carried out by Nernst, who discovered the remarkable fact that the thermal capacity of this substance tends practically to zero, even at the temperature $+ 50^\circ$ abs. Between this temperature and absolute zero, C_v or $\frac{dU}{dT} = 0$. We have already had occasion to point this out in connection with Nernst's heat theorem. From the shape of Einstein's curve (Fig. 5), it will be seen that C_p is tending towards zero at a temperature higher than 0° abs. It thus appears that, as far as the diamond is concerned, Einstein's theory reproduces experimental values with very considerable fidelity. While giving full weight to such general agreement, it is necessary to point out that this agreement is far from being complete in many other cases. We shall return,

to this after having described in outline the experimental methods of determining C_v and the characteristic vibration frequency ν .

Experimental Measurements of the Specific Heats of Solids, especially at Low Temperature.

(Cf. Nernst, *Journ. de Physique*, [4], **9**, 1910; Nernst, Koref, and Lindemann, *Sitzungsber. Berl. Akad.*, 1910, vol. 1, p. 247; *ibid.*, Nernst, p. 262; Nernst, *Annalen der Physik*, [4], **36**, 395, 1911.)

One form of calorimeter consisted of a heavy vessel of copper (about 400 grams in weight), the good thermal conductivity of such a mass of copper doing away with the necessity of stirring the substance, which is, of course, impossible in the case of solids. This was enclosed in a Dewar vacuum vessel, placed in a bath, the temperature of the calorimeter being measured by means of thermo-couples. The substance to be investigated was heated or cooled to a known temperature, and introduced into the calorimeter, the change in temperature of which was observed. Knowing the heat capacity of the calorimeter, the specific heat of the substance could be obtained. This method worked admirably, but of course it is limited to the determination of *mean* values of C_v , holding over a considerable temperature range. For the purposes in view, it was necessary, however, to be able to determine C_v for small temperature ranges, that is for a consecutive series of "points" on the temperature scale. To accomplish this, a different procedure had to be adopted.

The principle of this second method consists briefly in making the investigated substance itself act as its own calorimeter. The substance could be heated electrically by means of a platinum spiral, through which a known quantity of electrical energy was passed, as measured by an ammeter and voltmeter in the circuit. The rise in temperature of the substance was obtained by using the heating spiral itself as a resistance thermometer, *i.e.* its resistance was observed by means of a bridge, before and after the heating of the substance, the alteration in resistance giving the temperature change. Knowing the mass of substance employed, the electrical energy supplied, and the rise in temperature, it is easy to calculate the specific heat of the substance. This extremely ingenious method was worked out by Eucken, in Nernst's laboratory (*Physik. Zeitschr.*, **10**, 586, 1909), and has been employed by Nernst and his collaborators for the accurate determination of specific heats of substances at various temperatures, extending over a wide range, even down to the temperature of liquid hydrogen. A few details may be given here. A pear-shaped vessel of glass (shown in the accompanying figure, Fig. 6) contains the calorimeter K suspended by the wires which are connected to the heating spiral. By means of a Gaede pump, together with a vessel of charcoal cooled in liquid air, a very good vacuum is maintained in the glass vessel, so as to prevent any loss of heat by convection. The calorimeter K (*i.e.* the substance itself), together with the connecting wires, is brought to a certain temperature,

which is rapidly brought about by substituting hydrogen gas in place of air (since the hydrogen conducts thermally so much better). The hydrogen is subsequently removed, the vessel being evacuated. The spiral resistance is of purest platinum. Its change in resistance with temperature was calibrated by comparison with an oxygen gas thermometer. The calorimeter K varied in construction, according as to whether the substance investigated conducted heat well or badly. The first type shown in the figure is suitable when the substance is a metal. It consists of a small cylinder of the metal, having a cylindrical hole drilled almost throughout its length. Into this a plug of the same metal fits loosely, the heating spiral occupying the space between. To insulate the spiral thin paraffined paper was employed, liquid paraffin itself being finally poured in. The upper part of the plug is somewhat

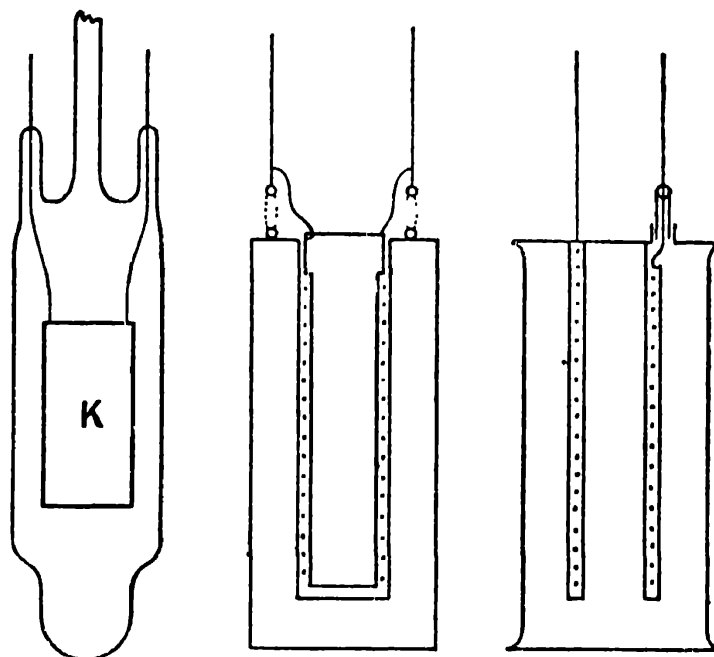


FIG. 6.

thicker than the remainder, good thermal contact being thus obtained. For substances which conduct heat badly the second form of calorimeter was employed. A vessel of silver was used, the platinum spiral being wound round a cylindrical sheet of silver, which served to spread the heat rapidly. Electrical insulation of the spiral was maintained by the help of shellac and thin silk. The platinum wire, on entering the calorimeter, passes through a small insulating tube, and finally, after passing through the body of the calorimeter, ends on the silver vessel, to which a lead is attached. It was found that some air must be left in the calorimeter itself (not in the pear-shaped vessel), so as to ensure better thermal conduction, and attainment of equilibrium. Nernst also describes a third form of calorimeter, suitable for liquids, details of which will be found in the paper cited. The heat capacity of the fittings of the calorimeter K—other than the actual substance examined—was

determined, and found to agree well with that calculated from the known masses and specific heats of the substances employed. When the pear-shaped vessel was well evacuated, the temperature of the substance, *i.e.* the calorimeter K (as measured by the resistance of the spiral) was found to remain remarkably constant for a considerable time, even when K had been previously cooled down to very low temperatures, by placing the non-evacuated pear-shaped vessel in contact with liquid air. Similarly, after cutting off the current the new (final) temperature was again found to remain constant, and be accurately measurable. Nernst considers that the probable error in the results does not exceed 1 per cent., and may be much less.

Some of the experimental data, obtained by the above means, have already been given in dealing with Nernst's heat theorem, and other examples will be given when we take up in greater detail the question of the applicability of Einstein's expression to the atomic heat of solids in general.

METHODS OF DETERMINING THE CHARACTERISTIC VIBRATION FREQUENCY OF A SOLID.

First Method.

This depends on the direct measurement of the "Reststrahlen (Residual Rays)." Many substances possess the property of selective reflection, that is they powerfully reflect rays of certain wave-length. The rays which are most strongly reflected in the case of *incident* light are those which are most strongly absorbed when the light is *transmitted*. The wave-lengths strongly absorbed are identical with the characteristic wave-lengths corresponding to the natural vibration frequencies of the substance, for it is when the light has the same frequency as that of the vibrating atom that it is most strongly absorbed. If a beam of incident light of all wave-lengths, that is to say, a beam emitted by a heated black body, is reflected successively from a number of pieces of the solid in question, at each reflection the beam will become purer, that is the reflected light tends more and more to consist of the vibration frequency characteristic of the solid. The rays which survive after having suffered a number of such reflections are called the "Residual Rays." The measurement of the wave-length and the energy of such Reststrahlen has been principally carried out by Prof. Rubens of Berlin and his collaborators, although the idea was that of Beckmann in the first instance (*cf.* Rubens and Nichols, *Annalen der Physik*, **60**, 418, 1897; Rubens and Aschkinass, *ibid.*, **65**, 241, 1898; Rubens, *ibid.*, **69**, 576, 1899; Rubens and Kurlbaum, *ibid.*, [4], **4**, 649, 1901; Rubens and Höllnagel, *Phil. Mag.*, [6], **19**, 761, 1910). These rays corresponding to the vibration frequency of atoms are naturally far in the infra-red region. The apparatus employed is shown diagrammatically in the figure (Fig. 7). L is the electrically heated black body emitting waves of all frequencies. D₁ and D₂ are diaphragms of small aperture. S is a screen. The diaphragms and screen are kept cool with water at room

temperature. The substance under examination is represented by P_1, P_2, P_3, P_4 . The surfaces of these pieces are polished as highly as possible. M is an adjustable mirror and T the thermopile. A diffraction grating of special make could be inserted in the path of the beam, thereby analysing it into a spectrum, the position of the energy maxima corresponding to the characteristic vibration frequencies of the substance P being determined by means of the thermopile. In later experiments the grating had to be abandoned owing to the large amount of absorp-

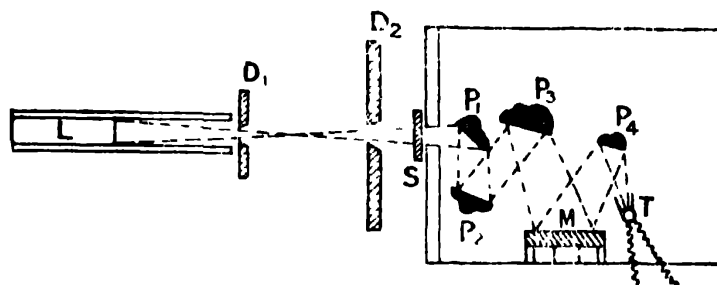


FIG. 7.

tion suffered by the rays in passing through it. Instead, an interference method has been devised—see the paper by Rubens and Hollnagel, *Phil. Mag.*, *l.c.* The following table contains some of the results summarised by Rubens and von Wartenberg (*Sitzungsber. konigl. preuss. Akad.*, 1914, p. 169). In actual experiment two bands are usually observed fairly close together. One of these, however, is due to the presence of water vapour (Rubens, *ibid.*, 1913, p. 513).

RESIDUAL RAYS CHARACTERISTIC OF CERTAIN SOLID SALTS.

Substance	Wave-Length in μ .		Wave-Length in μ .
NH_4Cl . .	51.5	AgCN	93 approx.
NaCl . . .	52.0	KI .	94.1
NH_4Br . .	59.3	HgCl_2	95 approx.
KCl	63.4	CaCO_3	98.7
AgCl . . .	81.5	Hg_2Cl_2	98.8
KBr	82.6	AgBr	112.7
PbCl_2 . . .	91.0	TlBr	117.0
TlCl	91.6	TlI	151.8

Second Method.

This is an indirect method due to Einstein (*Annalen d. Physik*, [4], 34, 170, 1911). From consideration of the distribution of atoms in metals and the forces acting upon them when they are displaced from their centres of gravity during vibration, Einstein obtained an approximate expression for the characteristic vibration frequency ν in terms of the compressibility K , the atomic (or molecular) volume V , and the atomic (or molecular) weight M , which may be written as follows:—

$$\nu = 2.54 \times 10^7 \frac{V^{\frac{1}{3}}}{M^{\frac{1}{2}} K^{\frac{1}{2}}}$$

Using Grüneisen's data for the compressibility (*Ann. der. Physik*, 25, 848, 1908), Einstein calculated the following characteristic vibration frequencies :—

SOME OF EINSTEIN'S VALUES FOR ν .

Substance.	ν	Substance.	ν .
Al . . .	6.6×10^{12}	Fe . . .	6.5×10^{12}
Cu . . .	5.7	Pt . . .	4.6
Ag . . .	4.1	Pb . . .	2.2
Au . . .	3.8	Cd . . .	2.6
Ni . . .	6.6	Bi . . .	1.8

Einstein himself does not claim that this method is more than a rough approximation. Nevertheless the values agree moderately well with those obtained by other methods.

Third Method.

This method, also an indirect one, is due to F. A. Lindemann (*Physikal. Zeitsch.*, 11, 609, 1910). It is based upon the assumption that *at the melting point T_s of a solid the amplitude of vibration of the atoms is approximately equal to the mean distance of the atoms apart.* Let us denote by r_s the radius of the circular vibration of an atom (in a metal, say), then the mean velocity u with which it vibrates is given by $u = 2\pi r_s \nu$, where ν is, of course, the number of such vibrations per second.

The mean kinetic energy of vibration is $\frac{1}{2}m u^2$, where m is the mass of the atom, and since there is likewise present an equal quantity of potential energy, the total mean energy of a vibrating atom is $m u^2$ or $4\pi^2 m r_s^2 \nu^2$. Now at the melting point the metals may be considered as very closely obeying Dulong and Petit's Law, *i.e.* their atomic heat is practically 6. That is, the expression for the vibrating energy which is given by—

$$U = \frac{3R}{N} \times \frac{\beta_0 T_s}{e^{\beta_0 \nu / T} - 1} \text{ reduces to } \frac{3RT_s}{N},$$

for large values of T as already pointed out.

$$\text{Hence} \quad 4\pi^2 m r_s^2 \nu^2 = \frac{3RT_s}{N},$$

$$\text{or} \quad \nu \propto \sqrt{\frac{T_s}{m r_s^2}}.$$

If we now regard the atomic volume V as proportional to the cube of the mean distance apart of the atoms (which distance is identical with r_s on Lindemann's assumption), we can write—

$$\propto \sqrt{\frac{T_s}{m V^{2/3}}}.$$

• The proportionality factor obtained by comparison with experiment is 2.80×10^{12} , and hence Lindemann's formula is—

$$= 2.80 \times 10^{12} \sqrt{\frac{T_s}{mV^{2/3}}}$$

It is thus possible to calculate ν from measurements of melting temperature, molecular weight of the atoms, and the atomic volume. This is an extremely convenient method, but has the disadvantage of not giving ν very accurately. It appears, however, to be somewhat more accurate than Einstein's method (Method 2). The following table is given by Nernst and Lindemann (*Z. Elektrochem.*, **17**, 822, 1911). The observed values of ν are those given by a formula of Nernst and Lindemann which is a modification of Einstein's expression for atomic heat, which at the same time represents experimental values more closely. We shall discuss this expression later, but in the meantime it may be taken as giving the values of ν from atomic heat measurements.

 LINDEMANN'S FORMULA FOR " ν ".

Substance.	Molecular Weight.	T _s Melting Point.	V Molecular Volume.	Calculated by Lindemann's Formula.	"Observed".
Al . .	27.1	930	10.0	7.6×10^{12}	8.3×10^{12}
Cu . .	63.6	1357	7.1	6.8	6.6
Zn . .	65.4	692	9.2	4.4	4.8
Ag . .	107.9	1234	10.3	4.4	4.5
Pb . .	206.9	600	18.3	1.8	1.9
Diamond	12.0	3600 ?	3.4	32.5	40.0
Iodine .	127.0	386	25.7	1.7	2.0
NaCl . .	29.2	1083	13.5	7.2	5.9
KCl . .	37.2	1051	18.9	5.6	4.5

Lindemann's formula, like Einstein's, gives only a single *mean* characteristic vibration frequency. For this purpose, therefore, the molecule of NaCl, KCl, etc., is treated as a single atom having an atomic weight one-half of that usually assigned to the *molecule* of these substances.

Fourth Method.

This method has also been suggested by Lindemann (*Ber. Deutsch. phys. Ges.*, **13**, 1107, (1911)). Lindemann has shown (*ibid.*, p. 482) that the characteristic ultra-violet frequency ν which enters into the selective photo-electric effect ¹ is given by the expression—

$$\nu_{\text{violet}} = \frac{1}{2\pi} \sqrt{\frac{ne^2}{mr^3}}$$

Cf. Chap. VI.

where n is the "valency," e the charge on an electron (in electrostatic units), m the mass of an electron, and r one half of the distance between the centres of two neighbouring atoms.

Lindemann introduces an expression due to Haber and discussed later (p. 190), which connects the ultra-violet frequency with the characteristic infra-red frequency, ν_{red} , the relation being—

$$\frac{\nu_{\text{violet}}}{\nu_{\text{red}}} = \sqrt{\frac{M}{m}}$$

where m is the mass of an electron, and M the actual mass of the atom. Combining this expression with that given above we obtain—

$$\nu_{\text{red}} = \frac{e}{2\pi} \sqrt{\frac{n}{Mr^3}}$$

Further, if A is the atomic weight, N the number of atoms in one gram-atom, and d the density of the substance, then Lindemann shows that—

$$r = \frac{\sqrt[6]{2}}{2} \sqrt[3]{\frac{A}{d \cdot N}}$$

Hence,

$$\nu_{\text{red}} = \sqrt[4]{2} \cdot N \cdot \frac{\sqrt{dn}}{A}$$

But $eN = F = \text{the Faraday} = 2.9 \times 10^{14}$ electrostatic units.

Hence,
$$\nu_{\text{red}} = 1.095 \times 10^{14} \sqrt{\frac{d}{A}}$$

By means of a suitable choice of n we can calculate the infra-red frequency of an element from this formula. The calculated values agree with those observed, in some cases better than do those values obtained by the melting-point method. There is a certain arbitrariness, however, in the choice of the valency n , as will be seen from the following table which is quoted from Lindemann's paper :—

Element	Lindemann Melting-point Formula.	$1.1 \times 10^{14} \sqrt{\frac{n \cdot d}{A}}$	ν "Observed".
Al .	7.6×10^{12}	8.2×10^{12}	8.3×10^{12}
Cu .	6.8	7.2	6.6
Ag .	4.4	4.6	4.4
Hg .	1.3	2.0	2.2
Pb .	1.8	2.5	1.9
Diamond	> 32.5	34.1	40.0
S .	3.9	6.6	7.3
I .	1.7	1.9	2.0

The weakness of the method lies in the selection of the value of the valency n of the element under consideration. Of the four methods mentioned, Lindemann's melting-point method is probably the most convenient; the most accurate method is undoubtedly the direct measurement of the frequency of the residual rays.

The System of Elements and the Periodicity of the Vibration Frequency with the Atomic Weights.

(Cf. W. Biltz, *Zeitsch. Elektrochem.*, **17**, 676, 1911.)

Employing Lindemann's formula, Biltz has calculated the characteristic vibration frequency ν for the elements (in the solid state) as far as the existing data upon melting point and density permitted, and has traced out a relation between the frequency and the atomic weight. In the following table are given the values of ν for each element as calculated by the help of Lindemann's formula¹ :—

Element	Density.	Melting-point Temperature T Absolute	Atomic Weight	$\nu \times 10^{-12}$
H	0.0763	14	1.01	4.36
He (liquid)	0.154	Ca 2	3.99	0.66
Li	0.59	459	6.94	10.0
Be	1.73	Ca 1200	9.1	18.5
C (graphite)	2.3	„ 3600	12.0	27.7
C (diamond)	3.52	„ 3600	12.0	31.7
N	1.03	62.5	14.0	2.5
O	1.43	28	16.0	1.7
F (liquid)	1.14	50	19.0	1.8
[Ne (liquid)	1.24	Ca 2	20.2	0.34
Na	0.98	371	23.0	3.96
Mg	1.74	924	24.3	7.2
Al	2.66	930	27.1	7.5
Si	2.49	1700	28.3	9.6
P (red)	2.34	903	31.0	6.3
S (rhombic)	2.07	388	32.1	3.96
Cl (liquid)	1.66	171	35.5	2.24
Ar (liquid)	1.42	85	39.9	1.32
K	0.87	335	39.1	2.3
Ca	1.59	1050	40.1	4.9
Ti	4.50	2120	48.1	8.4
Vd	5.8	1950	51.1	8.3
Cr	6.74	1790	52.0	8.3
Mn	7.39	1520	54.9	7.5
Fe	7.85	1820	55.9	8.3
Co	8.72	1780	59.0	8.2
Ni	8.90	1760	58.7	8.2
Cu	8.93	1357	63.6	6.7
Zn	7.12	692	65.4	4.36
Ga	5.95	303	69.9	2.5
Ge	5.47	Ca 1100	72.5	4.6
As	5.73	„ 1000	75.0	4.36
Se (grey)	4.8	490	79.2	2.7
Br (liquid)	3.19	266	79.9	1.7
Kr (liquid)	2.16	104	82.9	0.9
Rb	1.52	311	85.5	1.45
Sr	2.63	[1080]	87.6	3.0

¹ The values of ν are slightly different from those given by Biltz, as Biltz employed the older and less correct proportionality factor 2.12×10^{11} in Lindemann's formula instead of the later one, 2.80×10^{12} .

Element.	Density.	Melting-point Temperature T Absolute.	Atomic Weight.	$\nu \times 10^{-12}$
[Zr	6.4	Ca 2700	90.6	—
[Nb	7.8	2220	93.5	—
Mo	9.01	2400	96.0	6.3
[Ru	12.3	Ca 2256	102.0	—
Pd	11.9	1860	107.0	5.74
Ag	10.5	1234	108.0	4.36
Cd	8.65	595	112.0	3.0
In	7.12	428	115.0	2.1
Sn	7.30	505	119.0	2.24
Sb	6.62	904	120.0	3.0
Te	6.23	723	127.5	2.45
I	4.66	386	127.0	1.6
X (liquid)	3.52	133	130.0	0.85
Cs	1.89	299	133.0	0.95
Ba	3.78	1120	137.0	2.4
La	6.16	1085	139.0	2.8
Ce	7.04	896	140.2	2.64
Ta	16.6	2575	181	4.75
Os	22.5	2700	191	5.1
Ir	22.4	2500	193	4.9
Pt	22.5	2018	195	4.36
Au	19.3	1337	197	3.4
Hg	14.2	234	200	1.25
Tl	11.8	575	204	1.84
Pb	11.4	600	207	1.84
Bi	9.78	541	208	1.6
[Th	12.2	Ca 2100	232	3.2

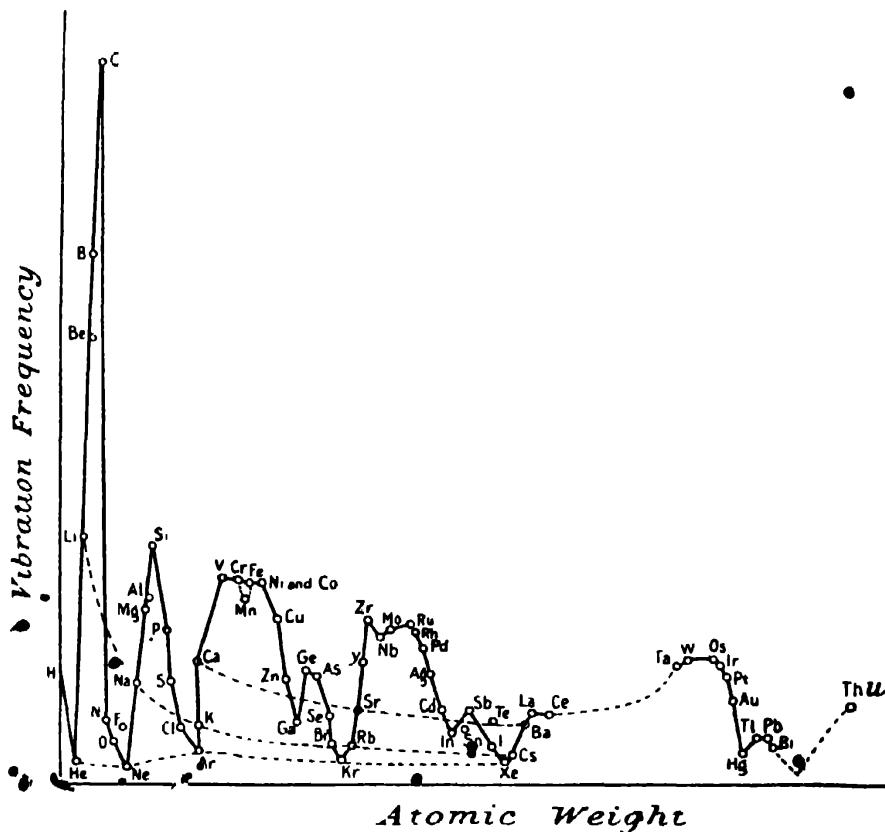


FIG. 8.

• Biltz points out that in the characteristic frequency we have a very fundamental atomic constant.* Further, since its measurement involves *two* properties, namely, specific volume and melting point, it is a step further than the stage reached, for example, in Lothar Meyer's curve, in which one property only is brought into relation to the atomic weight. Some doubt, of course, exists regarding the values in the case of a few elements, especially those possessing allotropic forms. Biltz has plotted the frequencies against the atomic weights, and has found the periodic variation shown in the figure (Fig. 8). It will be seen to be quite analogous to Mendeleef's original scheme. The majority of the elements occupy places on the curve, exceptions being fluorine, manganese, tin, and tellurium. Argon and potassium occupy as usual their anomalous position. The position of hydrogen, which was for a long time in doubt, is clearly that of the first member of the halogen series, as Ramsay had insisted on many years ago. The unique position of carbon, with extremely high value of ν , brings out very clearly its unique chemical character as regards its immense capability of forming compounds. An atom possessing high frequency no doubt is the most likely type of atom to allow of the transfer of electrons to and from itself, *i.e.* valency electrons.

Further Consideration of Einstein's Expression for Atomic Heat.

Einstein's expression, *viz.*—

$$C_v = 3R \frac{e^{\beta_0 \nu} \left(\frac{\beta_0 \nu}{T} \right)^2}{(e^{\beta_0 \nu / T} - 1)^3}$$

has been applied to several metals and solid salts. The following two examples, at low temperatures, given by Nernst and Lindemann (*Ztsch. Elektrochem.*, **17**, 818, 1911), are instructive:—

COPPER. $\beta_0 \nu = 240$.

Temperature, Absolute.	Atomic Heat (Observed).	Atomic Heat (Calculated).
86.0	3.38	3.31
33.4	0.538	0.234
22.5	0.223	0.023

POTASSIUM CHLORIDE. $\beta_0 \nu = 218$.

Temperature, Absolute.	Atomic Heat (Observed).	Atomic Heat (Calculated).
86.0	4.36	3.54
52.8	2.80	1.70
30.1	0.98	0.235
22.8	0.58	0.039

It is clear that while Einstein's formula gives the qualitative course of the variation of C_v with temperature, it is far from reproducing the variation quantitatively. It might be thought that this is due to an error in using a single frequency value where in the actual case there might be a broad band. From Rubens' results already quoted it will be seen, however, that the characteristic frequency of each salt is fairly isolated, and at lower temperatures this isolation would become still more perfect. In metallic elements themselves, where it is usually regarded that we are dealing with uncombined (unpolymerised) atoms themselves, the characteristic frequency should be quite sharp and well defined.

As a way out of the difficulty—prior to the publication of Debye's formula of 1912, to which reference will be made later—Nernst and Lindemann proposed an empirical expression for C_v , which differs somewhat from that of Einstein.

The Nernst-Lindemann Formula for the Atomic Heat of Solids.

This expression takes the following form:—

$$C_v = \frac{3}{2}R \left\{ \frac{\left(\frac{\beta_0 \nu}{T}\right)^2 \cdot e^{\beta_0 \nu / T}}{(e^{\beta_0 \nu / T} - 1)^2} + \frac{\left(\frac{\beta_0 \nu}{2T}\right)^2 \cdot e^{\beta_0 \nu / 2T}}{(e^{\beta_0 \nu / 2T} - 1)^2} \right\} \quad (1)$$

that is, the atomic heat expression of Einstein has been split up into two portions. One portion represents the energy corresponding to the characteristic frequency ν ; the second portion represents the energy due to the harmonic vibration, which is one "octave" lower than the characteristic, namely, $\frac{\nu}{2}$. Why this "octave" should be introduced is unexplained. The expression, however, reproduces the experimental value of C_v with extraordinary accuracy. Its importance is therefore not to be questioned. Some illustrations of its applicability may be given here.

First of all, we have to notice that the direct experimentally determined values of the atomic heat, such as those of Nernst and his collaborators, hold for constant pressure, *i.e.* they are (C_p) values. In the formula, however, it is the atomic heat at constant volume, *viz.* C_v , which occurs. They are nearly identical, but not quite. We have, therefore, to convert the one into the other. The procedure is as follows. On the basis of thermodynamics¹ we have the relation—

$$C_p = C_v \left(1 + \frac{9T\alpha^2 V}{K C_v} \right)$$

where α is the linear coefficient of expansion, V the molecular or atomic volume, and K the compressibility. Now experiment has shown that it is allowable to consider $\frac{V}{K}$ as a constant, independent of T (especially

¹ G. N. Lewis, *J. Amer. Chem. Soc.*, **29**, 1165 (1907).

as it occurs in a small correction term), and further, making use of Gruneisen's relation (*Verhandl. d. d. physik. Gesell.*, 1911, 491) regarding the proportionality between C_p and the expansion coefficient α , we can rewrite the above expression in the form—

$$C_p = C_v + C_p^2 \Gamma A^*$$

where A is a constant characteristic of each substance. The values of A are given in the following table for some metals and salts:—

VALUES OF THE CONSTANT "A".

Substance	Atomic Volume V	$3\alpha \times 1$	$K \times 10^{12}$	C_p/C_v	$A \times 10^5$
Al . . .	10.0	72	1.48	1.042	2.2
Cu . . .	7.1	48	0.785	1.025	1.3
Ag . . .	10.3	55	0.775	1.047	2.5
Pb . . .	18.3	82	2.4	1.055	3.0
Pt . . .	9.1	27	0.40	1.019	1.0
NaCl . .	13.5	121	4.28	1.051	2.7
KCl . . .	18.9	114	7.6	1.038	2.0

In the case of substances for which the compressibility K and the coefficient of expansion α are known, it is easy to convert C_v values into C_p , or *vice versa*. For other substances, however, the procedure is somewhat different. The individual constant A can be shown to be inversely proportional to the melting point T_s (*cf.* Nernst and Lindemann, *loc. cit.*). We can thus write $A = \frac{A_0}{T_s}$ where A_0 is a universal constant having the value 0.0214 (C.G.S. units). Hence—

$$C_p = C_v + C_p^2 \frac{T}{T_s} A_0$$

The general method adopted by Nernst and Lindemann to test their formula, equation 1, was, first of all, to calculate C_v by its means for substances for which ν is known (either by means of Reststrahlen measurements, or by means of Lindemann's melting-point formula). The "calculated" value of C_v was then converted into terms of C_p by means of the expression—

$$C_p = C_v + C_p^2 \Gamma A$$

and the result finally compared with the observed values of C_p .

The following tables give the results obtained in the case of aluminium, copper, silver, lead, and the salts KCl, NaCl, KBr, and the

* This expression has been recently transformed into a still simpler one, *viz.* $C_p = C_v + \alpha T^{3/2}$, where α is an empiric constant characteristic of the substance in question (Lindemann and Magnus, *Z. Elektrochem.*, 16, 26, 1910; *cf.* also Nernst, *Ann. Physik.*, 36, 3, 1911). Since direct measurement always gives us C_p , this is a very convenient way of getting C_v .

diamond. These are all taken from the paper of Nernst and Lindemann (*loc. cit.*):—

ALUMINIUM. $\beta_0\nu = 405$.

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed	Observer
32.4	0.23	0.23	0.25	Nernst.
35.1	0.31	0.31	0.33	"
83.0	2.42	2.43	2.41	"
86.0	2.52	2.53	2.52	"
88.3	2.61	2.62	2.62	"
137.0	3.99	4.05	3.97	Koref.
235.0	5.15	5.30	5.32	Koref, Schimpff.
331.0	5.52	5.76	5.82	Magnus, Schimpff.
433.0	5.70	6.06	6.10	Magnus.
555.0	5.80	6.30	6.48	"

COPPER. $\beta_0\nu = 321$.

T Absolute.	C_v Calculated.	C_p Calculated	C_p Observed	Observer.
23.5	0.15	0.15	0.22	Nernst.
27.7	0.31	0.31	0.32	"
33.4	0.59	0.59	0.54	"
87.0	3.35	3.37	3.33	"
88.0	3.37	3.39	3.38	"
137.0	4.60	4.65	4.57	Koref.
234.0	5.42	5.52	5.59	Koref, Schimpff.
290.0	5.60	5.75	5.79	Gaede.
323.0	5.66	5.81	5.90	Bartoli, Stracciati,
450.0	5.81	6.03	6.09	Schimpff.
				Magnus.

SILVER. $\beta_0\nu = 221$.

T Absolute	C_v Calculated	C_p Calculated.	C_p Observed.	Observer.
35.0	1.59	1.59	1.58	Nernst
39.1	1.92	1.92	1.90	"
42.9	2.22	2.22	2.26	"
45.5	2.43	2.44	2.47	"
51.4	2.81	2.82	2.81	"
53.8	2.97	2.98	2.90	"
77.0	4.07	4.11	4.07	"
100.0	4.72	4.77	4.86	Koref.
200.0	5.60	5.77	5.78	"
233.0	5.77	6.02	6.00	Koref, Schimpff.
331.0	5.82	6.12	6.01	Bartoli, Stracciati,
535.0	5.90	6.45	6.46	Schimpff.
589.0	5.92	6.57	6.64	Magnus.

LEAD. $\beta_0\nu = 95$.

T Absolute	C_v Calculated	C_p Calculated	C_p Observed	Observer.
23.0	2.95	2.96	2.96	Nernst.
28.3	3.63	3.64	3.92	"
36.8	4.35	4.37	4.40	"
38.1	4.43	4.45	4.45	"
85.5	5.60	5.68	5.65	"
90.2	5.62	5.70	5.71	"
200.0	5.90	6.12	6.13	Koref.
273.0	5.92	6.24	6.31	Koref, Gaede.
290.0	5.92	6.26	6.33	Gaede.
332.0	5.93	6.31	6.41	Magnus, Schimpff.
409.0	5.94	6.40	6.61	Magnus.

ATOMIC HEAT OF DIAMOND.

$\beta_0\nu = 1940$ (obtained by using Lindemann's formula, the melting point being taken as 3600°).

T Absolute	C_v Calculated	C_p Calculated	C_p Observed	Observer.
30	0.000	0.000	0.00	Nernst.
42	0.000	0.000	0.00	"
88	0.006	0.006	0.03	"
92	0.009	0.009	0.03	"
205	0.62	0.62	0.62	"
209	0.65	0.65	0.66	"
220	0.74	0.74	0.72	"
222	0.78	0.78	0.76	Weber.
232	0.87	0.87	0.86	Koref.
243	0.97	0.97	0.95	Dewar.
262	1.16	1.16	1.14	Weber.
284	1.37	1.37	1.35	"
306	1.59	1.59	1.58	"
331	1.82	1.83	1.84	"
358	2.07	2.08	2.12	"
413	2.53	2.55	2.66	"
1169	5.19	5.41	5.45	"

The agreement between theoretical and observed values is good. The important point about the diamond, as already remarked, is that it ceases to have any measureable heat capacity at all for about 40° above absolute zero. This is in agreement both with the thermodynamic theorem of Nernst and the Einstein theory of specific heat.

We now pass to the consideration of the salts KCl, NaCl, and KBr. Each of these possesses a single well-defined band in the far infra-red measured experimentally by Rubens. This value has been employed in the equation. The values of C_v and C_p are mean atomic heats, i.e. one half the molecular heats.

KCl. $\beta_0\nu = 218$.

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
22.8	0.61	0.61	0.58	Nernst.
26.9	0.70	0.70	0.76	"
30.1	1.23	1.23	0.98 ?	"
33.7	1.53	1.53	1.25 ?	"
39.0	1.98	1.98	1.83	"
48.3	2.66	2.66	2.85	"
52.8	2.96	2.97	2.80	"
57.6	3.25	3.26	3.06	"
63.2	3.57	3.59	3.36	"
70.0	3.85	3.87	3.79	"
76.6	4.10	4.13	4.11	"
86.0	4.40	4.43	4.36	"
137.0	5.26	5.33	5.25	Koref.
235.0	5.70	5.86	5.89	"
331.0	5.83	6.06	6.16	Magnus.
416.0	5.87	6.21	6.36	"
550.0	5.91	6.36	6.54	"

NaCl. $\beta_0\nu = 287$.

T Absolute.	C_v Calculated.	C_p Calculated.	C_p Observed.	Observer.
25.0	0.32	0.32	0.29	Nernst.
25.5	0.34	0.34	0.31	"
28.0	0.48	0.48	0.40	"
67.5	2.87	2.88	3.06	"
69.0	2.94	2.95	3.13	"
81.4	3.47	3.49	3.54	"
83.4	3.61	3.64	3.75	"
138.0	4.82	4.90	4.87	Koref.
235.0	5.52	5.73	5.76	"

KBr. $\beta_0\nu = 177$ (C_p was calculated from C_v by the usual formula, the value of A being taken as identical with that for NaCl).

T Absolute	C_v Calculated	C_p Calculated.	C_p Observed.	Observer.
78.7	4.67	4.70	4.74	Nernst
82.5	4.77	4.80	4.76	"
85.4	4.82	4.85	4.82	"
89.2	4.91	4.94	5.03	"
137.0	5.47	5.56	5.42	Koref
234.0	5.79	6.02	6.10	"

• The agreement between the observed mean atomic heat of these three salts and that calculated on the basis of the Nernst-Lindemann equation would appear to be thoroughly satisfactory. This, however, is really to a large extent accidental. Nernst found later that the Nernst-Lindemann equation would not apply to other salts. He was led ultimately to a different treatment of the problem of the mean atomic heat (or half molecular heat) of polyatomic substances which will be discussed briefly when we have become acquainted with the equation of Debye.

It should be pointed out that no very clear theoretical significance can be attached to the Nernst-Lindemann equation even when applied to monatomic substances. Its merit is that it reproduces experimental data in such cases with a high degree of accuracy, and in this respect is decidedly to be preferred to the equation of Einstein. The Nernst-Lindemann equation resembles Einstein's in that a single frequency ν , obtained by one of the methods mentioned previously, is employed, along with one half of this quantity.

The Specific Heat of Solids at High Temperatures and the Significance of the Energy possessed by the Electrons.

It will be remembered that the expression for the atomic heat (at constant volume) of a solid, whether stated in the original form of Einstein or in the Nernst-Lindemann modification, reaches as a limit the value $3R$ (5.95 cal.). As a matter of fact, however, the atomic heat (at *constant volume*) has been found to exceed this limit considerably when the temperature to which the value of the atomic heat refers is very high. At these temperatures there must be some other source of internal energy content not taken account of in simply ascribing the total energy to the vibrations of the *atoms*. At high temperatures the body becomes "white hot," that is, it is capable of emitting short waves in the *visible*, which are due in all probability (as we have already seen) to the vibrations of the *electrons* in the atoms. Although the energy of the electrons can be neglected at low temperatures compared with that possessed by the atoms, this is no longer the case at high temperatures, and hence such must be taken into account in any expression for specific (or atomic) heat. An attempt in this direction has been made by J. Koenigsberger (*Zeitsch. Elektrochem.*, **17**, 289, 1911), who considers that the atomic heat of metals (at constant volume) should reach 9 instead of 6, by taking the vibrating energy of the electrons into account. No great stress, however, can be laid upon the significance of the actual numerical limit quoted (*cf.* Nernst and Lindemann, *loc. cit.*). It is interesting, however, to see the numerical values for the atomic heat C_v actually obtained at high temperatures (*cf.* Koenigsberger, *loc. cit.*):—

ATOMIC HEAT (AT CONSTANT VOLUME) AT HIGH TEMPERATURES.*

Metal.	Region of Temperature	C_v	Observer.
Silver	907-1100° C.	6.7	Pionchon (1887).
Tin	1100°	9.2	"
Iron	1200°	9.6	"
Nickel	1150°	7.9	"
Copper	900°	7.1	Richards (1893).
Aluminium . .	650°	7.7	Boutchew.

DEBYE'S EQUATION FOR THE ATOMIC HEAT OF SOLIDS

(P. Debye, *Ann. Physik*, [iv.], **39**, 789, 1912.)

We have seen that Einstein's specific (atomic) heat formula only holds qualitatively, and that whilst that of Nernst and Lindemann accords much better with experiment, their expression suffers from the very serious drawback of lacking a sound theoretical basis. Debye has developed an expression having a theoretical basis—employing the quantum hypothesis—and has found that the expression reproduces experimental values with even greater fidelity than that of Nernst and Lindemann. Debye's formula may therefore be regarded as the most significant of all specific heat formulæ yet proposed. The general line of thought pursued by Debye is as follows:—¹

In Einstein's investigation it was assumed for the sake of simplicity that the vibrating particle (the atom) only gave rise to monochromatic radiation (frequency ν) and only absorbed such. Instead of this limitation to a single characteristic frequency ν , Debye works out the expression for atomic heat on the basis of absorption (and emission) of a number of vibration frequencies, in fact a whole spectrum. It will be seen at once that this is far more likely to coincide with what actually occurs than the simpler assumption of Einstein. Debye starts out with the very plausible assumption that a vibrating atom in a solid cannot be vibrating simply harmonically with a *single* frequency, but owing to the proximity of other atoms and probably to collisions with them the mode of vibration will be complex. Such complex modes of vibration can be treated, as Fourier showed, as theoretically made up of a *series* of true simple harmonic motions, and we have thus to integrate over a spectrum of frequencies if we wish to calculate with greater exactness the total energy content of a vibrating atom. The first point to be noted is, however, that we do *not* deal with a spectrum extending from $\nu = 0$ to $\nu = \infty$. If a body consists of N atoms—treated as massive points—the system possesses $3N$ degrees of freedom. The system will therefore in general exercise $3N$ different periodic vibrations, *i.e.* $3N$ different vibration frequencies. If the older view—consonant with the principle of *equipartition* of energy—were true, namely, that the energy

*†. ¹ For details see Debye's paper. Also Appendix II.

was the same for each degree of freedom over the entire spectrum, then we could state directly that each vibration frequency corresponded to the energy kT (where $k = \frac{R}{N}$, N being now the number of atoms in 1 gram-atom), so that the total energy of the body would be simply $3NkT$ per gram-atom as Dulong and Petit's Law requires.

We have seen, however, that the whole point of the quantum theory is the negation of the principle of equipartition throughout a spectrum, and that instead the energy per vibration varies with the type of vibration. This lack of equipartition is expressed, as we have already seen, in the Planck expression $\frac{h\nu}{e^{h\nu/kT} - 1}$, which gives the true mean energy of any single vibration ν . To obtain the total energy of the vibrating system it is necessary to sum this expression over the spectrum (of absorption or emission), the spectrum not containing an infinite number of frequencies but limited to $3N$, as already pointed out. The spectrum is characterised by two factors: (a) its boundaries, (b) the density of the lines, i.e. the number of lines in any given vibration region $d\nu$. There is, according to Debye, a certain definite limiting frequency ν_m beyond which the spectrum does not extend. Debye has reached a number of important conclusions in the course of his investigation. The first is this: *If the temperature T be regarded as a multiple (or submultiple) of a temperature θ (a characteristic constant for any given substance), then the atomic heat for all monatomic substances can be represented by the same curve, i.e. the atomic heat is a universal function of $\frac{T}{\theta}$.*

A second relation which is not confined to monatomic substances states that *the number of lines spread over a region $d\nu$ is proportional to $\nu^2 d\nu$* (a relation for black-body radiation already obtained by Jeans). From this Debye concludes that *at sufficiently low temperatures the atomic heat of all solids is proportional to T^3 , that is to the third power of the absolute temperature.* This conclusion differs (theoretically) widely from the conclusion of the Einstein and the Nernst-Lindemann equations. It is borne out by the experimental data, but experiment at low temperature bears out the Nernst-Lindemann view equally. As a corollary it follows that *the atomic energy content at low temperatures is proportional to the fourth power of the absolute temperature* (cf. Stefan's Law for total radiation). Debye's expression for the energy U of a solid of volume V which contains N atoms is—

$$U = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu}{e^{h\nu/kT} - 1} \cdot \nu^2 d\nu \quad (1)$$

the energy not being ascribed to a single harmonic vibration ν , but to a spectrum of such extending from 0 to ν_m . If we now define the temperature θ (the characteristic constant of the substance) by the expression—

$$\theta = \frac{h\nu_m}{k} = \beta\nu_m \quad (2)$$

and introduce into equation (1) as a new dimensionless variable—the magnitude—

$$\xi = \frac{h\nu}{kT} \quad (3)$$

we can write—

$$U = 9NkT \left(\frac{kT}{h\nu_m} \right)^3 \int_0^{\frac{h\nu_m}{kT}} \frac{\xi^3 d\xi}{e^\xi - 1} \quad (4)$$

or, substituting θ for $\frac{h\nu_m}{k}$, we obtain—

$$U = 9NkT \left(\frac{T}{\theta} \right)^3 \int_0^{\frac{\theta}{T}} \frac{\xi^3 d\xi}{e^\xi - 1} \quad (5)$$

Dulong and Petit's Law, if true, would require the relation—

$$U = 3NkT.$$

Now if we write $\frac{\theta}{T} = x$, and differentiate equation (5) with respect to temperature, we obtain finally—

$$C_v = 3Nk \left(\frac{12}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3x}{e^x - 1} \right) \quad (6)$$

The magnitude $3Nk$ has the value 5.955 cal. and may be denoted by C_∞ since this numerical limit is reached at high temperatures. Equation (6) may therefore be rewritten in the form—

$$\frac{C_v}{C_\infty} = \frac{12}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3x}{e^x - 1} \quad (7)$$

Equation (6) or (7) is Debye's atomic heat formula.

For the case in which x is *small*, i.e. T is large (compared to θ), $\frac{\xi^3}{e^\xi - 1}$ becomes ξ^2 , and $\frac{3x}{e^x - 1}$ becomes $\frac{3x}{x}$ or simply 3. Hence, $\frac{C_v}{C_\infty} = \frac{12}{3} - 3 = 1$, in other words, Dulong and Petit's Law holds at high temperatures. On the other hand, when x is *large*, i.e. T is small, we obtain by expanding $\int_0^\infty \frac{\xi^3 d\xi}{e^\xi - 1}$ the series $\xi^3(e^{-\xi} + e^{-2\xi} + e^{-3\xi} + \dots)d\xi$, or—

$$6 \left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \frac{1}{4^4} + \dots \right).$$

Hence equation (7) yields—since the series expression in the bracket is 1.0823—

$$\frac{C_v}{C_\infty} = 12 \times 6 \times 1.0823 = 77.938 \frac{T^3}{\theta^3}$$

That is, at sufficiently low temperatures, the atomic heat is proportional to the cube of the absolute temperature T . (The above relation can be used to calculate θ , employing the experimental value of $\frac{C_v}{C_\infty}$ at some low temperature.)

Debye has tested his formula (equation (6) or (7)) and found it to agree very well with experiment. It has further been tested independently by Nernst and Lindemann (*Sitzungsber. Berl. Akad.*, p. 1160, 1912) with the following results, in which the values of C_p (atomic heat at constant pressure) are obtained from the values of C_v given by Debye's formula by employing one of the relations between C_p and C_v mentioned at an earlier stage. Nernst and Lindemann slightly alter the form of Debye's equation (in respect of the symbols) so as to bring it more into line with previous expressions. The expression as used by them takes the form—

$$C_v = 3R \left[\frac{4\pi^4}{5} \left(\frac{T}{\beta_v} \right)^3 - \frac{3}{n} \frac{T}{\beta_v} - 12 \frac{\beta_v}{T} \sum e^{-\frac{n^2 \beta_v}{T^2}} \left\{ \frac{1}{n^2 \beta_v} + \frac{3}{n^2 \left(\frac{\beta_v}{T} \right)^2} + \frac{6}{n^3 \left(\frac{\beta_v}{T} \right)^3} + \frac{6}{n^4 \left(\frac{\beta_v}{T} \right)^4} \right\} \right]$$

ALUMINIUM ($\theta = \beta_v = 398$; earlier value employed = 405).

T.	C_p Observed.	C_p Calculated.	Difference Obs.-Calc. (Formula of Debye).	Difference Obs.-Calc. (Formula of Nernst and Lindemann).
32.4	0.25	0.25	0.00	+ 0.02
35.1	0.33	0.32	+ 0.01	+ 0.02
83.0	2.41	2.36	+ 0.05	- 0.02
86.0	2.52	2.50	+ 0.02	- 0.01
88.3	2.62	2.59	+ 0.03	0.00
137.0	3.97	4.10	- 0.13	- 0.08
235.0	5.32	5.34	- 0.02	+ 0.02
331.0	5.82	5.78	+ 0.04	+ 0.06
433.0	6.10	6.07	+ 0.03	+ 0.04
555.0	6.48	6.30	+ 0.18	+ 0.18

DIAMOND ($\beta\nu = 1860$; earlier value 1940).

T.	C_p Observed.	C_p Calculated.	Difference Obs.-Calc. (Formula of Debye)	Difference Obs.-Calc. (Formula of Nernst and Lindemann).
88	0.025	0.049	- 0.021	+ 0.022
92	0.033	0.058	- 0.025	+ 0.024
205	0.618	0.61	+ 0.008	0.00
209	0.662	0.66	+ 0.002	+ 0.001
220	0.722	0.74	- 0.018	- 0.04
222	0.76	0.75	+ 0.01	- 0.02
243	0.95	0.925	+ 0.025	- 0.02
262	1.14	1.10	+ 0.04	- 0.02
284	1.35	1.32	+ 0.03	- 0.02
306	1.58	1.54	+ 0.04	- 0.01
331	1.84	1.82	+ 0.02	+ 0.001
358	2.12	2.07	+ 0.05	+ 0.04
413	2.66	2.61	+ 0.05	+ 0.11
1169	5.45	5.49	- 0.04	+ 0.04

SILVER ($\beta\nu = 215$; her value employed = 221).

	C_p Observed.	C_p Calculated.	Difference Obs.-Calc. (Formula of Debye).	Difference Obs.-Calc. (Formula of Nernst and Lindemann).
35.0	1.58	1.50	+ 0.08	- 0.001
39.1	1.90	1.88	+ 0.02	- 0.02
42.9	2.26	2.14	+ 0.12	+ 0.04
45.5	2.47	2.42	+ 0.05	+ 0.03
51.4	2.81	2.85	- 0.04	- 0.001
53.8	2.90	3.02	- 0.12	- 0.08
77.0	4.07	4.19	- 0.12	- 0.04
100	4.86	4.83	+ 0.03	+ 0.09
200	5.78	5.80	- 0.02	+ 0.001
273	6.00	6.04	- 0.04	- 0.02
331	6.01	6.13	- 0.12	- 0.11
535	6.46	6.46	0.0	+ 0.001
589	6.64	6.57	+ 0.07	+ 0.07

Copper gave an equally satisfactory result. On the whole Debye's equation applies more exactly even than the equation of Nernst and Lindemann. Debye's equation has of course the further advantage that it possesses a theoretical basis, whilst that of Nernst and Lindemann is semi-empirical.

NOTE on the method of evaluating the summation term of the Debye formula in the form given by Nernst and Lindemann.

To evaluate—

$$\sum_{n=1}^{\infty} e^{-n\frac{\beta\nu}{T}} \left(\frac{1}{nT} + \frac{3}{n^2(\frac{\beta\nu}{T})^2} + \frac{6}{n^3(\frac{\beta\nu}{T})^3} + \frac{6}{n^4(\frac{\beta\nu}{T})^4} \right)$$

Set $\frac{\beta\nu}{T}$ equal to x . Also set $e^{-1} = a$. Then $e^{-nx} = a^n = (a^1)^n = y^n$ if y be set equal to a^1 .

The sum can therefore be written :

$$\sum_{n=1}^{\infty} a^n \left(\frac{1}{n\lambda} + \frac{3}{n^2\lambda^2} + \frac{6}{n^3\lambda^3} + \frac{6}{n^4\lambda^4} \right)$$

or the same expression may be written :

$$\begin{aligned} & \sum_{n=1}^{\infty} a^n \cdot \frac{1}{n\lambda} + \sum_{n=1}^{\infty} a^n \cdot \frac{3}{n^2\lambda^2} + \sum_{n=1}^{\infty} a^n \cdot \frac{6}{n^3\lambda^3} + \sum_{n=1}^{\infty} a^n \cdot \frac{6}{n^4\lambda^4} \\ & \underbrace{\sum_{n=1}^{\infty} a^n \cdot \frac{1}{n\lambda}}_{\text{First term}} + \underbrace{\sum_{n=1}^{\infty} a^n \cdot \frac{3}{n^2\lambda^2}}_{\text{Second term}} + \underbrace{\sum_{n=1}^{\infty} a^n \cdot \frac{6}{n^3\lambda^3}}_{\text{Third term}} + \underbrace{\sum_{n=1}^{\infty} a^n \cdot \frac{6}{n^4\lambda^4}}_{\text{Fourth term}} \\ & \text{First term} = \frac{1}{\lambda} \left[y + \frac{y^2}{2} + \frac{y^3}{3} + \dots \text{ad inf.} \right]. \\ & \text{Second term} = \frac{3}{\lambda^2} \left[\frac{y}{1^2} + \frac{y^2}{2^2} + \frac{y^3}{3^2} + \frac{y^4}{4^2} + \dots \text{ad inf.} \right]. \\ & \text{Third term} = \frac{6}{\lambda^3} \left[\frac{y}{1^3} + \frac{y^2}{2^3} + \frac{y^3}{3^3} + \frac{y^4}{4^3} + \dots \text{ad inf.} \right]. \\ & \text{Fourth term} = \frac{6}{\lambda^4} \left[\frac{y}{1^4} + \frac{y^2}{2^4} + \frac{y^3}{3^4} + \frac{y^4}{4^4} + \dots \text{ad inf.} \right]. \end{aligned}$$

Each of these series is convergent, so that only the first three or four expressions in each need be taken into account.

Characteristic Infra-red Frequencies Obtained From Debye's Formula.

—By means of equation (2) of the preceding section it is possible to calculate the characteristic infra-red frequency $\nu_{\max}$ (which represents the upper limit of the spectrum of vibrations) from a determination of the characteristic temperature θ . This temperature can be obtained in turn from the elastic constants of the substance as has been shown by Debye. Making use of Debye's values of θ , H. S. Allen (*Proc. Roy. Soc., A*, **94**, 100 (1917)) has calculated $\nu_{\max}$ for the elements given in the following table. It will be observed that the frequencies so obtained agree very well with those calculated by methods previously mentioned:—

Atomic Frequencies by Debye's Formula.

Al	8.26
Fe	9.67
Ni	9.01
Cu	6.81
Pd	4.22
Ag	4.39
Cd	3.48
Sn	3.83
Pt	4.68
Au	3.41
Pb	1.49
Bi	2.30

In dealing with the molecular heats of solids and their variation with temperature, it is necessary in certain cases to make allowance for the existence of allotropic change which will in general involve a heat effect. It is necessary to know the magnitude of this heat effect and the temperature of transition as otherwise serious error may enter into the value ascribed to the molecular heat. The existence of more than one solid form has been demonstrated in cases in which perhaps it would not have been anticipated. Thus Eucken (*Ber. Deutsch. phys. Ges.*, **18**, 4 (1916)) has found that solid nitrogen can exist in two forms, the transition temperature being 35.5° abs. and the molecular latent heat of transition 53.8 cal. Oxygen exhibits three solid forms, having the transition temperatures, 23.5° and 42.5° abs. respectively, the corresponding latent heats being 17.5 and 167.4 cal per mole. Carbon monoxide exists in two forms, the transition temperature being 60.4° abs. and the molecular latent heat of transition 144.1 cal.

MOLECULAR HEATS OF POLYATOMIC SOLIDS, E.G. SALTS.

It has already been mentioned that the Nernst-Lindemann equation does not take account of the molecular heats of salts in general, although it appears to do so for KCl, NaCl, and KBr. The Debye equation is equally inapplicable. Nernst proceeds therefore in the following manner:—

In the case of a polyatomic molecule in a *solid* there are two types of vibration to be considered; first, the vibration of the molecule as a whole, and secondly, the vibration of the atoms inside each molecule. This view, it will be observed, is difficult to reconcile with the conclusion arrived at, as a result of Bragg's work on crystals by the X-ray method, according to which molecules of simple binary salts, though not more complex molecules, lose their identity in the solid state. Nevertheless the method employed by Nernst in connection with molecular heats of salts, etc., is highly successful, and must be considered, although an open mind has to be kept regarding certain of the assumptions. According to Nernst the mode of vibration of the *molecules* is taken account of by Debye's formula, whilst that of the *atoms* is taken account of by Einstein's formula. It is reasonable to treat the motion of atoms inside a molecule as closely analogous to that of the atoms in a monatomic solid, to which case Einstein's formula was intended to apply in the first instance. Nernst's method amounts therefore to a combination of Einstein's and Debye's formulæ. The frequency ν_1 , *i.e.* the upper frequency employed in the Debye portion of the expression, is obtained from the melting-point formula of Lindemann, whilst the frequency ν_2 employed in the Einstein portion of the expression is that given directly by the Reststrahlen method.¹

¹ ν_2 is greater than ν_1 ; hence at low temperatures there are practically no resonators possessing the quantum $h\nu_2$. That is, at low temperatures the *atoms* possess scarcely any energy of vibration whilst the *molecules* as a whole do possess energy of vibration.

On adding the two portions together the resulting expression gives the whole molecular heat of the solid. If C_v denotes, as before, the mean atomic (or half molecular) heat of a diatomic solid such as KCl, then $2C_v$ denotes the whole molecular heat of the solid at constant volume, and according to Nernst—

$$2C_v = F_1\left(\frac{\beta_{v_1}}{T}\right) + F_2\left(\frac{\beta_{v_2}}{T}\right)$$

where F_1 and F_2 are the Debye and Einstein functions or atomic heat expressions respectively.

In the case of KCl, $\beta_{v_1} = 166$ (obtained from the melting-point formula), and $\beta_{v_2} = 213.5$ (obtained directly from the Reststrahlen observations). The following table, taken from Nernst's *Theory of the Solid State*, gives the values of the Einstein and Debye portions of the molecular heat in the case of KCl. The column headed "correction" contains the quantities which must be added to $2C_v$ in order to give $2C_p$, the molecular heat at constant pressure:—

$$\text{KCl. } \beta_{v_2} = 213.5; \beta_{v_1} = 166.$$

T.	Einstein.	Debye.	Correction.	Sum ($2C_p$ Calc.)	$2C_p$ Obs.
22.8	0.046	1.04	—	1.086	1.16
26.9	0.13	1.48	—	1.61	1.52
30.1	0.25	1.87	—	2.12	1.96
33.7	0.43	2.25	—	2.68	2.50
48.3	1.13	3.52	—	4.95	5.70
57.6	2.13	4.06	0.02	6.21	6.12
70.0	2.89	4.57	0.04	7.50	7.58
86.0	3.66	4.97	0.06	8.79	8.72
235	5.55	5.81	0.32	11.68	11.78
416	5.83	5.91	0.68	12.42	12.72
550	5.87	5.93	0.90	12.70	13.18

$$\text{NaCl. } \beta_{v_2} = 282; \beta_{v_1} = 229 \text{ (215).}$$

T.	Einstein	Debye.	Correction.	Sum.	$2C_p$ Obs.
25	0.010	0.610	—	0.62	0.58
25.5	0.012	0.637	—	0.65	0.62
28.0	0.027	0.794	—	0.82	0.80
67.5	1.65	3.56	0.02	5.23	6.22
69.0	1.73	3.63	0.02	5.38	6.26
81.4	2.39	4.13	0.04	6.56	7.08
83.4	2.49	4.20	0.06	6.75	7.50
138	4.26	5.22	0.16	9.64	9.74
235	5.29	5.68	0.42	11.39	11.52

$$\text{AgCl. } \beta\nu_2 = 179; \beta\nu_1 = 102 (114).$$

T.	Einstein.	Debye.	Correction	Sum.	$2C_p$ Obs.
23.6	0.17	2.78	—	2.95	2.98
26.4	0.31	3.18	—	3.49	3.44
32.8	0.76	3.89	0.04	4.69	4.79
45.6	1.90	4.69	0.97	6.78	7.25
87.0	4.24	5.58	0.18	10.00	9.74
116	4.92	5.75	0.28	10.95	10.34
207.5	5.59	5.90	0.52	12.01	11.81
330	5.81	5.93	1.3	13.04	13.01
405	5.85	5.94	1.8	13.59	13.60
430	5.86	5.94	1.9	13.70	13.72

The numbers in brackets denote the values of $\beta\nu_1$ actually obtained by the melting-point method. They are very close to the values of $\beta\nu_1$ which are arbitrarily chosen.

An examination of the data given shows that at very low temperatures the contribution made by the Debye portion is much greater than that made by the Einstein portion, as we would expect.

It will be recalled that the Nernst-Lindemann formula applies fairly well to the case of KCl and NaCl, the frequency employed being that obtained by the Reststrahlen method. "This agreement must be regarded as half accidental, and may be explained on algebraic grounds from the approximation—

$$2R \left(\frac{\beta_1}{T} \right) = 0.75 \frac{\beta_1}{T} + F_2 \left(\frac{\beta_1}{T} \right)$$

In the case of KCl and NaCl the fundamental [molecular] frequency [ν_1 in the above table] is in fact about 0.75 times the internal [atomic] frequency [ν_2 in the above case]."

An interesting case is that of mercurous chloride. Taking the molecular formula to be HgCl and calculating the molecular heat by the above method, discrepancies are observed which lie outside experimental error. Nernst concludes, therefore, that in solid calomel the molecule Hg_2Cl_2 (and possibly a still more complex molecule) exists, which is in agreement with conclusions arrived at concerning the molecular formula of calomel in the dissolved state. "The exact complexity cannot yet be decided since the melting point of the salt is not open to observation on account of decomposition."

A further interesting case is that of ice. In order to account for the molecular heat of ice by the above method it is necessary to regard the molecular weight as 36 approximately (*cf.* Nernst, *The Theory of the Solid State*). Graphite and sulphur likewise show evidence of considerable polymerisation.

Although the method of treatment which has just been outlined is very ingenious, it is obviously of a somewhat hypothetical character in

its present formulation. It is not improbable that considerable modifications may eventually be introduced. It represents, however, a partially successful attempt to solve the problem of the heat capacity of polyatomic substances.

Latimer (*Journ. Amer. Chem. Soc.*, **44**, 90, 1922) has determined the molar heats of the tetrachlorides of carbon, silicon, titanium, and tin, these being chosen as belonging to the same type and differing only in the mass of the central metallic atom. The equation of Debye was found to apply more or less closely. Dealing with the applicability of Debye's equation to solid compounds, Latimer points out that whilst metals in general follow the regular Debye curve the specific heats of compounds in general do not. Latimer does not agree with the mode of treatment outlined above. He regards the typical Debye curve as representing "the manner in which a *single* atom gains thermal energy and only when all the atoms of a substance are of similar mass and are held by similar constraints will the C_v curve for the substance be of the same form. Hence for a compound such as mercurous chloride, even though both the mercury and chlorine atoms gain thermal energy according to this typical curve, the C_v curve for the mercury will lie above that for the chlorine, and the C_v curve for the compound, which must be the average of the two, will deviate from this typical curve. On the other hand, the C_v curve for potassium chloride agrees very closely with the regular curve due to the close agreement of the masses of the potassium and chlorine atoms. Examples of the quantitative agreement of the average specific heat curves with the mean of two Debye curves could be given for many substances. In the case of the tetrachlorides, the curves for silicon and titanium should follow the shape of the regular Debye curve very closely. The greatest deviation is to be expected with tin tetrachloride, but since there are four chlorine atoms to one atom of tin, even in this case, the error introduced in assuming the regular curve for extrapolating over the low temperature should not be very great."

CHAPTER IV.

Energy content of gases—Molecular heats of gases—Infra-red absorption spectra of gases—Degradation theory of gases.

IN Chapter I. we have already had occasion to discuss briefly the problem of the molecular heats of gases. It has been pointed out that the observed values cannot be accounted for on the basis of the equipartition principle, especially the fact that the molecular heat varies with the temperature. In view of the considerable advance which has been made possible in the analogous case of solids by the application of the quantum theory, it is of interest to see how far the same considerations can be applied in the present case. This problem was first taken up by Bjerrum (*Zeitsch. Elektrochem.*, **17**, 731 (1911); *ibid.*, **18**, 101 (1912)).

In Chapter I. we have given a table showing the number of possible degrees of freedom, as estimated by Bjerrum, which are possessed by mono-, di-, tri-, and tetra-atomic gas molecules in respect of translation, rotation, and vibration. In the case of monatomic gases, which appear to possess translational energy only, the equipartition principle of classical statistical mechanics gives a satisfactory explanation of the observed values, e.g. the case of argon already discussed. So long as we restrict ourselves to translational movement the equipartition principle necessarily holds good, whether the molecule be monatomic or polyatomic; the distribution of energy in terms of the quantum theory only enters when we deal with vibrations or, as we shall see later, with rotations of the molecule as a whole. For the present, however, we are not applying the quantum theory to molecular rotations but to atomic vibrations alone. It will be recalled that rotational energy is practically entirely kinetic (*cf.* Chap. I.).

In regard to vibration of one atom with respect to the other in a diatomic gas molecule, according to the quantum hypothesis the sum of the kinetic and potential energies, instead of being RT , is a fraction ϕ of this quantity. That is the total vibrational energy is ϕRT . ϕ is a function of the temperature T and of the vibration frequency ν . According to Nernst and Lindemann we have—

$$\phi = \frac{1}{2} \frac{\beta \nu / T}{e^{\beta \nu / T} - 1} + \frac{1}{2} \frac{\beta \nu / 2T}{e^{\beta \nu / 2T} - 1}.$$

Bjerrum has investigated the Einstein function as well. It is found to hold fairly well, but is not so exact as that of Nernst and Lindemann.

At absolute zero ϕ is zero, and at high temperatures ϕ approximates to unity, *i.e.* at high temperatures the conclusions based on classical statistical mechanics ought to hold good.

In the case of a triatomic molecule, containing the atoms A, B, and C, these may vibrate with respect to one another in pairs, *viz.* A with respect to B, B with respect to C, and C with respect to A. There are therefore three different vibrations to be taken account of, and the total vibrational energy is—

$$RT(\phi_1 + \phi_2 + \phi_3).$$

The following tables contain the data obtained in the case of a number of gases. The wave-length λ is that chosen by Bjerrum for substitution in the Nernst-Lindemann equation. The temperature T is in degrees absolute. $C_v(x^\circ, T^\circ)$ denotes the *mean molecular* heat (at constant volume) over the temperature range between x° abs. and T° abs.

Molecular Heat of Hydrogen.

The formula employed by Bjerrum is :—

$$C_v(x^\circ, T^\circ) = (5/2) \cdot R + R\phi[2 \cdot 0\mu]$$

where $5/2R$ covers the translational and rotational energy¹ of the molecule and $2 \cdot 0\mu = \lambda$ is the characteristic wave-length of atomic vibration, which is of course connected with the frequency of atomic vibration by means of the relation $c = \lambda\nu$, where c is the velocity of light. The following table indicates the degree of agreement between the observed and calculated molecular heats of hydrogen :—

	C_v (291°, T°) Calculated.	C_v (291°, T°) Observed.
1734	5.39	5.23
2083	5.51	5.44
2431	5.62	5.68
2647	5.69	5.76

¹ Bjerrum, as already pointed out, ascribes two degrees of freedom to a diatomic molecule, such as H_2 , in respect of rotation of the molecule as a whole. By writing the corresponding energy term as RT (which then added to the $3/2RT$, due to translation, makes in all $5/2RT$), Bjerrum is here assuming that rotational energy may be treated from the standpoint of the equipartition principle. To get the contribution which translation and rotation make to the total molecular *heat* it is of course necessary to differentiate with respect to T , *i.e.* we obtain the term $5/2R$. The same assumption of equipartition is employed in the other gases, the molecular heats of which are considered. In a later paper, however (*Nernst Festschrift*, 1912, p. 90, Bjerrum regards rotational energy of the molecule as a quantity which has to be treated from the quantum standpoint (a view first suggested by Nernst, *Zeitsch. Elektrochem.*, 17, 265, 1911), the characteristic wave-length of molecular rotation lying far in the infra-red region (about 30μ in the case of hydrogen), whilst the characteristic wave-length of atomic *vibration* (inside the molecule) lies in the short infra-red region, between 1 and 10μ approx. In other words, molecular rotations are much less violent than atomic vibrations and require a much smaller quantum, *i.e.* a much smaller ν or greater λ .

Molecular Heat of Nitrogen. (Oxygen and carbon monoxide have the same molecular heat as nitrogen.)

Formula employed : $C_v(0^\circ, T^\circ) = (5/2) \cdot R + R\phi[2.4\mu] \dots$

T Abs.	$C_v(273^\circ, T^\circ)$ Calculated.	$C_v(273^\circ, T^\circ)$ Observed.
473	4.97	4.73
903	5.12	4.91
1273	5.32	5.25
1620	5.47	5.31
	$C_v(291^\circ, T^\circ)$ Calculated.	$C_v(291^\circ, T^\circ)$ Observed
1792	5.55	5.43
2057	5.65	5.58
2225	5.71	5.79
2446	5.78	5.87
2640	5.84	5.93

In the case of hydrogen the characteristic wave-length assumed for the atomic vibration is $\lambda = 2.0 \mu$; in the case of nitrogen, $\lambda = 2.4 \mu$. One would expect that if the vibrating particles are electrically charged an absorption band should occur at these positions in the case of hydrogen and nitrogen. No bands, however, have been observed in this region of the spectrum. On the other hand, oxygen and carbon monoxide have the same molecular heat as nitrogen, and direct measurement has shown that oxygen possesses bands at 3.2μ and 4.7μ , whilst carbon monoxide exhibits bands at 1.573μ , 2.35μ , these being "harmonics" of the fundamental band at 4.67μ (*cf.* Schaeffer and Thomas, *Zeitsch. Physik*, **12**, 330, 1923). The bands of oxygen are weak, and it is possible that hydrogen would exhibit a band if its absorption were measured when the gas itself were excited, *i.e.* at a fairly high temperature.

Whilst diatomic gases such as hydrogen, oxygen and nitrogen, possess atomic vibration frequencies which belong to the very short infra-red region, *viz.* 2 to 3μ , this is not the case for a gas such as chlorine which possesses a higher molecular heat than the gases just mentioned. Thus, at 0°C. , C_v for chlorine is 5.85, which becomes 7.4 at 2000°C. Ascribing the full (equipartition) value to the translational and rotational terms, namely $(3/2)R + R = 4.97$, we see that, even at 0°C. , chlorine exhibits a molecular heat which is sensibly affected by the atomic vibrational term to the extent: $5.85 - 4.97 = 0.88$. This quantity (0.88) is due to vibration having one degree of freedom. To make it comparable with the vibrational term of a solid we should have to imagine it multiplied by 3, that is equivalent to an atomic heat of 2.64 at 0°C. , if chlorine were a monatomic solid. On inspecting the values of vibrational frequencies already given in the case of solids it will be seen that an atomic heat of 2.64 at 0°C. requires a frequency

somewhat lower than that of the diamond, the value of the frequency in the latter case being 3×10^{13} which is equivalent to a wave-length of 10μ ; in fact the frequency required by the chlorine to account for its vibrational energy term would correspond to about 12μ when expressed in wave-length. This value is borne out by the molecular heat values at temperatures higher than 0°C . We would expect therefore that chlorine should exhibit an absorption band in the region of 12μ . The characteristic band exhibited by chlorine and attributed to atomic vibration is stated to occur at 4.3μ . There is a very considerable discrepancy in this case and we can scarcely regard it as an isolated one. On the whole our knowledge of the molecular heats of gases is not satisfactory, being much less exact than it is in the case of the atomic heats of solids.

Molecular Heat of CO_2 . (SO_2 has the same molecular heat.)

As this is a triatomic molecule we have three atomic vibrations to take account of. Two of these, however, may be expected to be the same, as the oxygen atoms are presumably linked symmetrically to the carbon atom. The translational energy plus the rotational energy are in this case, according to Bjerrum, represented by the term $3RT$, *i.e.* $(3/2)RT$ translational and $(3/2)RT$ rotational. The wave-length corresponding to the vibration frequency of each of the oxygen atoms with respect to the carbon is taken by Bjerrum to be 5.0μ ; the wave-length corresponding to the vibration of the two oxygen atoms against each other is taken to be 8.1μ . The formula employed by Bjerrum is—

$$C_v(0^\circ, T^\circ) = 3R + 2R\phi[5.0\mu] + R\phi[8.1\mu].$$

[Note that the second term on the right-hand side of this expression contains the number 2, to allow for the fact that there are two similar kinds of atomic vibrations present. It may also be pointed out that if CO_2 were a linear molecule, $\text{O} = \text{C} = \text{O}$, the rotational energy term would be RT (as in a diatomic gas). The fact that the value $3/2RT$ for the rotational energy agrees with experiment (*cf.* the following table) means that CO_2 is not a linear molecule, its spatial

constitution being represented approximately by $\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$. The con-

stitution of the CO_2 molecule is considered in detail by Bjerrum (*Verh. d. D. phys. Ges.*, **16**, 737, 1914).]

T Abs.	$C_v(273^\circ, T^\circ)$ Calculated.	$C_v(273^\circ, T^\circ)$ Observed.	$C_v(273^\circ, T^\circ)$ Calculated employing the Wave Lengths $2.7, 4.3,$ and 14.7μ .
473	7.44	7.48	7.67
903	8.67	8.60	8.47
1273	9.35	9.33	9.00
1637	9.80	9.84	9.40
1884	10.03	9.98	9.62
2112	10.21	10.28	9.81
2383	10.43	10.47	10.04

The agreement between observed and calculated values is satisfactory. We have now to see what evidence is available from the absorption spectrum of CO_2 as regards the choice of the wave-lengths employed. Direct measurement has shown that CO_2 possesses bands at $14\cdot7$, $4\cdot3$, and $2\cdot7\mu$. These are of the same order of magnitude as those used in the above formula. As a matter of fact, Bjerrum has also used the three observed values of λ and has obtained values for C_p which agree moderately with the observed. The formula in this case is—

$$C_p(o^\circ, T^\circ) = 3R + R\phi[2\cdot7\mu] + R\phi[4\cdot3\mu] + R\phi[14\cdot7\mu].$$

The resulting values are given in the last column of the preceding table.

Molecular Heat of Water Vapour.

The formula employed by Bjerrum is—

$$C_p(o^\circ, T^\circ) = 3R + 2R\phi[1\cdot3\mu] + R\phi[3\cdot6\mu] + \left(\frac{T}{3100}\right)^4.$$

The following values are thereby obtained :—

C_p , Calculated.			Remarks.
			These values are true molecular heats, <i>i.e.</i> instantaneous values for the temperatures referred to, not mean values over a wide range of temperature.
323	6.62	5.96	
543	6.34	6.10	
723	6.67	6.80	
	$C_p(383^\circ, T^\circ)$ Calculated	$C_p(383^\circ, T^\circ)$ Observed	
893	6.55	6.51	Mean values for the molecular heat over the temperature range indicated.
1273	6.95	6.95	
1600	7.36	7.40	
	$C_p(291^\circ, T^\circ)$ Calculated.	$C_p(291^\circ, T^\circ)$ Observed.	
2084	7.91	7.92	Ditto.
2383	8.54	8.54	
2650	9.14	9.37	
2936	9.9	10.0	
3181	10.7	10.5	
3337	11.3	10.9	

The absorption spectrum of water vapour contains many bands over the range of λ 's employed above, *i.e.* bands at $1\cdot1$, $1\cdot5$, $2\cdot0$, $3\cdot2$, $4\cdot7\mu$, etc. Where there are so many bands almost any value might be regarded as borne out by the absorption spectrum. It appears from this and other cases that the calculated molecular heat is not very sensitive to error in the actual value chosen for λ . The term $\left(\frac{T}{3100}\right)^4$ is a purely

empirical term introduced by Bjerrum to account for the fact that the molecular heat of water vapour increases with the temperature more rapidly than would be anticipated on the basis of the quantum theory. The cause of this is by no means clear: possibly it is connected with a depolymerisation of any bimolecules which may be present, though at the higher temperatures this would be a negligible quantity.

The molecular heat of ammonia, a tetra-atomic body, may likewise be calculated more or less satisfactorily by writing down terms for translation and rotation, and by applying the quantum theory to the vibrations of the atoms, using the wave-lengths 2.1μ and 8.9μ which actually occur in the absorption spectrum of ammonia.

It is evident from the foregoing that to account for the observed values of the molecular heats of gases it is essential to introduce the quantum theory in some form. Bjerrum's mode of treatment, though marking a considerable advance, is open to criticism, more particularly as regards the choice of the number of degrees of freedom.

One point remains to be emphasised in connection with the molecular heat, or rather the energy content of gases. Owing to the fact that the true atomic vibrations inside the molecule correspond to relatively high frequencies (*i.e.* short infra-red region) such vibrations contribute a relatively small amount to the total energy content; for as the frequency is high very few molecules will possess even one quantum of this type of energy. The so-called rotational frequencies (obtained on applying the quantum theory to rotation) are much more important as they occur in the longer infra-red region. We have already assigned a maximum value to the rotational contribution by applying the principle of equipartition to rotations.

The Absorption Spectrum of Water Vapour and of Gaseous Hydrogen Halides in the infra-red region from the point of view of Molecular Rotations, treated on the basis of the Quantum Theory.

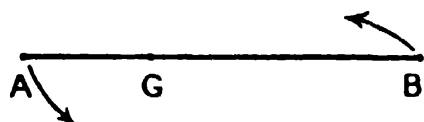
On examining the absorption spectrum of a gas in the infra-red region it is found in general that a number of bands occur at intervals not only in the short infra-red portion— 1μ to 10μ —but likewise at a series of positions in the far infra-red, in fact as far as direct measurements have as yet been carried (down to 270μ about). Owing to the very large magnitude of the interatomic forces holding the atoms together in a diatomic, or in general a polyatomic, gas molecule it may be anticipated that the vibratory motions of the atoms will possess a relatively high frequency, that is, the atomic vibrations are likely to be the source of the absorption bands in the *short* infra-red region. This is now very generally accepted. Use has already been made of this assumption by Bjerrum in connection with the molecular heats of gases. We have still to find, however, a source for the numerous bands exhibited by a gas in the far infra-red region. These were first definitely attributed to *rotations* of the molecule as a whole by Bjerrum in 1912 (*Nernst Festschrift*, p. 90). It is usual therefore to speak of the bands lying in the far infra-red as

constituting the "rotational spectrum" of the gas. That the quantum theory might be applied to rotations at all was first suggested by Nernst (*Zeitsch. Elektrochem.*, **17**, 265, 1911).

As rotations are regarded as having their origin in molecular collisions it would follow on classical statistical considerations that rotations of all values were possible, that is, that rotational energy would vary continuously for precisely the same reason that the translational energy of the molecules composing a gas varies continuously. One would predict indeed, on the basis of Maxwellian distribution, that the rotational energy lying within certain narrow limits would be the most probable. But this is very different from ascribing to molecules, as is done in quantising the rotations, certain special rotational frequencies, in fact, a series of such frequencies, distinct from one another, as this treatment implies that intermediate frequencies for some reason are impossible. To treat rotations therefore as being capable of quantisation is a bold step which happens to be justified rather by the results to which it leads than by any *a priori* process of reasoning.

Bjerrum's treatment is briefly as follows: In the first place, it is assumed that a molecule in a given rotational state is characterised by a number n where n denotes that the rotational frequency is n times the fundamental or lowest rotational frequency ν_0 . Suppose that the actual frequency of rotation is ν_r then we can write $\nu_r = n\nu_0$. According to Bjerrum n takes on the consecutive values 1, 2, 3, etc. On the older quantum theory employed by Bjerrum the energy of an oscillator (possessing potential as well as kinetic energy) is written as a whole number of quanta. Since the motion considered in rotations is kinetic only the energy of rotation should be represented by a whole number of "semi-quanta," that is by $n h \nu_r / 2$. At the same time it is known that the energy of rotation of a molecule can be written as $\frac{1}{2} I (2\pi\nu_r)^2$, where I is the moment of inertia¹ of the rotating system. For the sake of simplicity Bjerrum assumes that in the case of the water molecule the

¹ The moment of inertia of, say, a diatomic gas molecule is defined as follows: Consider two particles atoms A and B separated by a fixed distance l and rotating in the plane of the paper about their common centre of gravity G with an angular velocity ω radians per second ($\omega = 2\pi\nu$). Suppose that the masses of the atoms are m_A and m_B respectively. The kinetic energy of A is given by $\frac{1}{2} m_A \times (\text{linear velocity})^2$. The linear velocity is the length $\bar{AG}$ multiplied by ω . Further, the length $\bar{AG}$ is related to the distance l (i.e. the distance apart of the atom centres) by the expression—



$$\bar{AG} = l \times m_B / (m_A + m_B).$$

This follows from the fact that G is the centre of gravity and that, therefore, $m_A \times \bar{AG} = m_B \times \bar{BG}$, and also $l = \bar{AG} + \bar{BG}$. Hence—

$$\text{kinetic energy of A} = \frac{1}{2} m_A \cdot \omega^2 \cdot l^2 \cdot \left(\frac{m_B}{m_A + m_B} \right)^2$$

$$\text{and kinetic energy of B} = \frac{1}{2} m_B \cdot \omega^2 \cdot l^2 \cdot \left(\frac{m_A}{m_A + m_B} \right)^2$$

moment of inertia is the same for all axes through the centre of gravity, so that we are concerned with only one such term. Equating the two expressions for the energy of rotation we have :—

$$\frac{1}{2}I(2\pi\nu_r)^2 = \frac{1}{2}nh\nu_r$$

whence $\nu_r = nh/4\pi^2I$.

[Note.—Bjerrum writes the general expression for ν_r as, $\nu_r = nh/2\pi^2I$, on the basis that the energy of rotation (although entirely kinetic) can be equated to a whole number of quanta. For the purpose of dealing with series relationship in spectra the discrepancy is unimportant. It becomes of importance of course in any attempt to calculate the absolute value of I from spectroscopic data.]

On the above basis we would expect a series of values of ν_r according as n takes on the values 1, 2, 3, etc. It is important to observe that ν_r is the frequency of rotation of the molecular oscillator itself and in applying the above expression to account for spectra (*i.e.* absorption bands in the far infra-red) Bjerrum identifies the frequency of the radiation absorbed with the frequency of rotation in question. This mode of treating an oscillator is in agreement, so far as it goes, with the original concept of the Planck oscillator; it is wholly different from the mechanism of emission and absorption of radiation as visualised in the concept of Bohr (Chapter V.). Bjerrum's work preceded that of Bohr, however. In Chapter V. the rotation spectrum of a gas will be considered again in terms of Bohr's theory. It may also be emphasised that Bjerrum considers that when a molecule is characterised by n it possesses n quanta of the type or frequency ν_r , that is, its energy is $n^2h\nu_0$. With the slight modification introduced above the same idea is adhered to, the energy of rotation being written in general as $nh\nu_r/2$ or $n^2h\nu_0/2$.

On the above basis the lowest possible frequency is given by—

$$\nu_0 = h/4\pi^2I.$$

From an examination of the spectrum of water vapour Bjerrum has concluded that the frequency difference in the series of rotational bands is 1.73×10^{12} which ought to be identical with $h/4\pi^2I$. The wave-length corresponding to this frequency is 174μ which, on the basis of Bjerrum's computation, should be the longest wave-length due to molecular rotation.

It may perhaps be pointed out that the most probable rotational frequency—that is the most intense band—is not at all likely to be the lowest or fundamental frequency. As already pointed out, one would expect that the collisions with other molecules would result in a most

So that the total kinetic energy of rotation of the diatomic molecule

$$= \frac{1}{2}m_A \cdot m_B \cdot l^2 \cdot \omega^2 \cdot / (m_A + m_B).$$

But the total kinetic energy = $\frac{1}{2}I\omega^2$.

Therefore

$$I = \frac{m_A \cdot m_B}{m_A + m_B} \cdot l^2.$$

probable frequency of rotation which when quantised would be an integral multiple of ν_0 . Bjerrum indicates that in the case of water vapour the most probable rotation is $3\nu_0$.

Taking up the question of accounting for the series of bands exhibited by water vapour in the infra-red region Bjerrum first proceeds to consider the spectrum between the limits 10μ and 20μ , ascribing all the band heads therein to rotations, n being given consecutive values from 10 to 16. The corresponding wave-length series (in μ) is given by the expression—

$$\lambda = \frac{3 \times 10^{11}}{n \times 1.73 \times 10^{12}} \quad \frac{3 \times 10^{11}}{1.73 \times 10^{12}}$$

The following table indicates the degree of concordance obtained by this means.

Calculated.	10.8	11.6	12.4	13.3	14.4	15.8	17.3 ν
Observed	10.9	11.6	12.4	13.4	14.3	15.7	17.5 ν

With increasing wave-length the bands become deeper and tend to overlap. For wave-lengths greater than 17.5μ the absorption becomes general and without structure unless very good dispersion is obtained in the apparatus. Whilst these results are to be regarded as a considerable step in our understanding of the problem of the source of bands, the numerical results just quoted are, according to E. von Bahr, open to a certain amount of doubt (*Verh. d. D. phys. Ges.*, **15**, 731 (1913)).

One of the most striking features of the rotational origin attributed to the bands of the far infra-red region consists in the indication which it gives of the general *complex* character which should be manifested by an absorption band due to atomic *vibration*. As already pointed out atomic vibration of itself would be expected in the case of gaseous molecules to give rise to a band in the *short* infra-red region. Bjerrum was the first to apply certain considerations of Lord Rayleigh to the case of the vibrational band exhibited by water vapour in the neighbourhood of 6μ .

Lord Rayleigh pointed out (*Phil. Mag.* [V.], **24**, 410 (1892)) that if we are dealing with a *vibrating* particle, say an atom, vibrating with a frequency ν , and if this particle forms part of a molecule which is at the same time rotating round an axis *perpendicular* to the linear vibrations, then we would expect in general to find that the emission or absorption manifested by the molecule due to the compounding of the atomic vibration with the molecular rotation referred to, would consist of two lines having frequencies ν_1 and ν_2 where $\nu_1 = (\nu + \nu_r)$ and $\nu_2 = (\nu - \nu_r)$ respectively, where ν_r is the rotation frequency of the molecule, only one frequency of rotation being assumed. If, on the other hand, the molecule rotates *around* the line of atomic vibration the molecular rotation will have no effect on the atomic vibration, so that the molecule in which this

is happening will emit or absorb a single line of frequency ν . Since the first case must correspond to the actual behaviour of at least some of the molecules we would expect to find two lines symmetrically placed with respect to ν , and if ν itself is also present the short infra-red band would consist of three lines in all. What is actually observed is that the absorption band in the short infra-red is much more complex, being broad and consisting of numerous lines closely packed together. These lines are grouped more or less symmetrically around a central position. The central position should correspond to the vibrational frequency ν , but actually this frequency is apparently absent. Hence with a spectrometer of moderate dispersing power what is observed is a "double-headed" band, the wave-lengths of the "heads" being λ_1 and λ_2 . E. von Bahr suggests that the middle band is not really missing, but only apparently so, on account of insufficient dispersion. The two wave-lengths λ_1 and λ_2 , which in general lie fairly close together, correspond to two frequencies ν_1 and ν_2 , and their difference ($\nu_2 - \nu_1$) is just twice the most probable frequency ν_r of the rotation. ν_r is of course considerably smaller than either ν_1 or ν_2 and its normal position is far in the infra-red. On expressing ν_r in terms of its wave-length λ_r we find that $\lambda_r = 2 \frac{\lambda_1 \cdot \lambda_2}{\lambda_1 - \lambda_2}$. The above is a convenient way of measuring the rotational wave-length without having to investigate the far infra-red region.

At sufficiently high temperatures the energy of rotation should be directly proportional to the absolute temperature. Hence the frequency of rotation will be directly proportional to the square root of the temperature, since the rotational energy expression $\frac{1}{2}I(2\pi\nu_r)^2$ involves ν_r . Hence the product of a rotational wave-length into $\sqrt{T}$ should be a constant.

The validity of the expression can of course be tested by comparison with actual measurements in the far infra-red where the bands are due to rotation only. From what has been said above, it follows that the product $\frac{\lambda_1 \cdot \lambda_2}{\lambda_1 - \lambda_2} \cdot \sqrt{T}$ should be a constant, provided the theoretical considerations are sound. Making use of some data obtained by Paschen in the region 5 to 6 μ in the case of water vapour, E. von Bahr has found that the two heads of the double band (due to molecular rotations compounded with atomic variation) alter their relative position in accordance with the above expression.

$T^{\circ}\text{C.}$	λ_1	λ_2	$\sqrt{T} \frac{\lambda_1 \cdot \lambda_2}{\lambda_1 - \lambda_2}$	10.
17	6.512	5.948	1.17	•
100	6.527	5.900	1.19	
600	6.563	5.607	1.14	
1000	6.597	5.416	1.08	
• 1470	6.620	• 5.377	1.20	

In view of the fact that the temperature measurements were not very exact, the constancy of the expression in the last column is very satisfactory.

E. von Bahr has investigated more closely the constitution of the bands of water vapour between 5 and 6μ and has found that each exhibits a number of sub-maxima. Similar behaviour is shown by other gases. That is, the *discontinuous* nature of the absorption required by the quantum theory is fully borne out. Bjerrum regards the consecutive lines or sub-maxima in the short infra-red band as due to the compounding of the frequency ν (the true atomic vibrational frequency) with the consecutive series of rotational frequencies, ν_0 , $2\nu_0$, $3\nu_0$, etc., having their actual individual existence in the longer infra-red region. Since ν_0 is small compared with ν the single frequencies represented by $(\nu + \nu_0)$, $(\nu + 2\nu_0)$, $(\nu - \nu_0)$, $(\nu - 2\nu_0)$, etc., will lie fairly closely round the position ν itself, so that we obtain the appearance of a broad band in place of a single fine line in the short infra-red region. It will be observed that the frequency differences between consecutive sub-maxima in the broad band referred to is ν_0 . That is, we have, on the basis of Bjerrum's theory, a method of computing ν_0 and consequently harmonics thereof. From measurements of the positions of the successive sub-maxima it is found in the case of water vapour that the largest value for λ_r is of the order 400μ , *i.e.* water vapour should exhibit absorption at various positions down to this region, a result in agreement with the observations of Rubens. On the other hand, the experimental results obtained by E. von Bahr indicate a lack of symmetry with respect to the principal maximum of a given band, which indicates in turn that a *single* frequency difference is insufficient to account for the whole series of band heads.

The question of the rotational spectrum of water vapour, *i.e.* the infra-red spectrum beyond 10μ , has also been investigated by Eucken (*Verh. d. D. phys. Ges.*, **15**, 1159 (1913)). Eucken emphasises the lack of symmetry of the water molecule and ascribes to it at least two principal moments of inertia, which would lead us to expect two different series in the spectrum. Sackur (*Ann. physik.*, [iv.], **40**, 95, (1913)) has arrived at the conclusion—on quite other grounds—that the water molecule possesses two main moments of inertia, which are in the ratio of $1:2$. On taking two values for I , one of which is approximately twice the other, and calculating the corresponding series as given by the Bjerrum expression, one may compare the degree of agreement which is obtained between the calculated and observed band maxima. The results are recorded in the following table. In the first column are given the rotational wave-lengths directly observed by Reubens and his collaborators (*Sitzungsber. Preuss. Akad.*, p. 8, 1921). In the second and third columns are the data obtained from an analysis of the structure of the 6.26μ (atomic vibration) band of water vapour, which band, as already pointed out, consists of a number of sub-maxima distributed on both sides of a central position (6.26μ), which central position, however, corresponds rather remarkably not to a maximum but to minimum ab-

sorption. The most reliable data regarding this band are those of Sleator (*Astrophys. J.*, 48, 124, 1918). Sleator not only observed a number of sub-maxima—each of which is ascribed to rotation and vibration compounded—but even succeeded in showing that each sub maximum itself possessed a fine line structure. We are not concerned at present, however, with the structure of each sub-maximum but simply with

INFRA-RED ABSORPTION BANDS OF WATER VAPOUR.

Wave-length in μ observed directly by Rubens.	Wave-length in μ cal- culated from the Struc- ture of the 6.26μ Band.		Wave-length calculated on Rotation Theory			
	Col. 2.	Col. 3.	Col. 4.		Col. 5	
	E. von Bahr, Langley, Rubens, Hettner.	Sleator.	Bjerrum Series ($1 = 0.96 \times 10^{-40}$). n.		Eucken Series ($1 = 2.21 \times 10^{-40}$). n.	
19.2	19.3		19.3	9	19.1	21
19.7	19.9		—	—	20.0	20
20.5	20.6		—	—	21.0	19
21.6	21.8		21.6	8	—	—
22.9	23.3				22.2	18
23.8	24.3				23.5	17
25.0	25.2	25.3	24.7		25.0	16
26.6	26.9	26.9	—		26.7	15
28.9	28.3	28.9	28.9		28.5	14
30.6	30.6	30.6	—		30.7	13
32.9	32.9	34.2	—		33.3	12
35.7	35.7	36.7	34.7		36.3	11
40.0	38.8	40.3	—		40.0	10
—	42.0	43.0	43.3		—	
44.1	45.0		—		44.5	
—	47.5		—		—	
49.0	49.5	51.0	—		50.0	
57.7	55.0	56.8	57.8		57.1	
65.8	62.5	65.3	—		66.7	
72.2	69.5	72.5	—		—	
78.0	80.0	81.6	—		80.0	
(83)		—	—			
(92)		92.5	86.6			
		101	—			
105.8	109	—	—			
—	—	113	—			
132.2	126	135	—		133	3
175.6	171		173		—	—
—	—				200	2
265.7	240-250				—	—
	385-398				400	1

the location of the heads of the various sub-maxima, for the individual rotational wave-lengths, recorded in the table, and extending down through a great part of the far infra-red region are calculated from the differences in position of the successive sub-maxima clustered together and constituting the complex 6.26μ band; the heads of successive sub-maxima being measured in *frequencies* the successive frequency differences

are converted into the wave-lengths recorded. The fourth column of the table contains the rotational wave-lengths calculated by Bjerrum ascribing to the moment of inertia the value 0.96×10^{-40} , this value being obtained in turn from the frequency difference taken as a true constant, *viz.* 1.73×10^{12} . The fifth column contains the data calculated by Eucken on the basis that 400μ represents the longest rotational wave-length possible for the water vapour molecule, which number requires that I should be 2.21×10^{-40} , so that the fourth and fifth columns together constitute the rotational wave-lengths based on two moments of inertia of the water molecule. The region 10.9μ to 17.5μ is not included as the data have been given in a previous table.

It will be observed that the longest wave-length of the Eucken series, namely 400μ , is much greater than the region so far examined (1922) by the direct experimental method of Rubens. As Rubens points out the agreement between calculated and observed results is better in the short infra-red region than it is in the far infra-red. In his opinion there is probably a third series to be taken into consideration due to a very small electrical moment of the molecule perpendicular to the corresponding rotation axis.

The effect of this would not be observable directly in the far infra-red but would markedly influence the fine structure of the short wave band, with the result that the rotational wave-lengths calculated therefrom would not correspond very exactly with those directly observed.

It may be pointed out, however, that Sleator's values (with two exceptions) may be calculated with considerable accuracy if we take the longest rotational wave-length to be 404.8μ (*i.e.* $\nu_0 = 7.41 \times 10^{11}$) instead of 400μ , the value employed by Eucken. On this basis, using the expression: $\nu_0 = h/4\pi^2 I$, we find $I = 2 \times 10^{-40}$, and the following series of bands is obtained:

λ (Sleator)	—	135	101	81.6	65.3	57.7 (Rubens)	51
λ (calculated in μ)	404.8	202.4	134.9	101.2	81.0	67.5	57.8
<i>n</i>	1	2	3	4	5	6	7

λ (Sleator)	—	45 (von Bahr)	40.3	36.7	34.2	30.6	28.9	26.9	25.3
λ (calculated in μ)	45.0	—	40.5	36.8	33.7	31.7	28.9	27.0	25.3
			10	11	12	13	14	15	16

The above series, however, has the same limitations as that of Eucken, namely that for the region of wave-lengths shorter than 25μ it will lead to a large number of bands lying very close together; for this region it is necessary to take into account at least one other moment of inertia, giving a series such as that of Bjerrum for this region. That the water molecule has at least two moments of inertia is undoubtedly. But there

is another important consideration somewhat analogous to Rubens' comment given above, namely that the moment of inertia is probably not quite constant, but varies somewhat with the speed of rotation. The extension of Bjerrum's expression in this sense is obviously necessary—compare the more recent work on the hydrogen halides discussed later.

The Hydrogen Halides.

The absorption spectra of HCl , HBr , and HF in the infra-red region are of interest because of the greater simplicity in behaviour to be anticipated in these cases as compared with the behaviour of an unsymmetrical structure such as the water molecule.

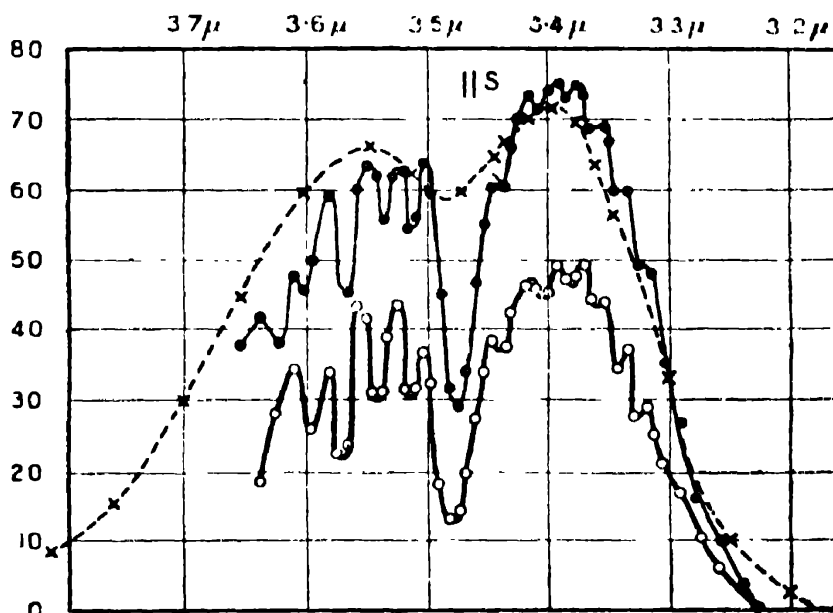


FIG. 9.—Hydrogen chloride gas (E. von Bahr). S denotes slit width. Dotted curve due to Burmeister. Upper full curve corresponds to 760 mm.; lower full curve corresponds to 380 mm.

E. von Bahr (*Verh. Deutsch. phys. Ges.*, **15**, 1154, 1913) has examined in some detail the infra-red absorption spectrum of HCl which exhibits a complex “double-headed” band with its centre at 3.474μ . The subdivision of each part of the double band (found by Burmeister and shown by the dotted line in the figure) into twelve separate maxima is very clearly shown in Fig. 9.

The data corresponding to Fig. 9 are given in the following table. The wave-lengths λ_1 and λ_2 of the right and left parts of the double absorption band, as well as the corresponding frequencies, are given. The first column contains the value of n , i.e. the order of that maximum reckoned from the middle of the absorption band. The middle of the absorption band is characterised by the wave-length $\lambda = 3.474\mu$, and the frequency $\nu = 8.636 \times 10^{12}$.

HYDROGEN CHLORIDE GAS.

n.	λ_1 in μ .	λ_2 in μ .	$\nu_1 \times 10^{-13}$.	$\nu_2 \times 10^{-13}$.
1	3.444	3.504	8.711	8.562
2	3.416	3.528	8.782	8.503
3	3.394	3.556	8.839	8.436
4	3.372	3.583	8.897	8.373
5	3.352	3.610	8.950	8.310
6	3.332	—	9.004	—
7	3.317	—	9.044	—

In the following table are given the values of $(\nu_1 - \nu)$ and $(\nu - \nu_2)$, which, according to Bjerrum, should be equal to the rotational frequencies of the molecule of HCl:—

	$\nu - \nu_2 \times 10^{-13}$			λ_r in μ .	
1	7.5	7.4	7.45	403 = λ_0	7.45
2	14.6	13.3	13.95	215	6.98
3	20.3	20.0	20.15	149	6.72
4	26.1	26.3	26.20	115	6.55
5	31.4	32.6	32.0	94	6.40
6	36.8	—	36.8	82	6.13
7	40.8	—	40.8	74	5.83

On Bjerrum's theory we would expect ν/n to be constant. As a matter of fact it is moderately constant over a considerable range but shows a definite tendency to diminish as n increases. E. von Bahr regards the variation as outside the limit of experimental error, although Eucken (*loc. cit.*) considers the question as not yet definitely settled. By employing the Bjerrum theory it is seen that HCl should absorb at several positions down to $\lambda = 400\mu$. Rubens and von Wartenberg (*Verh. d. D. phys. Ges.*, **13**, 796 (1911)) have found considerable absorption exhibited by this substance in the residual-ray range, the absorption being especially strong at 150μ .

Bjerrum (*Verh. d. D. phys. Ges.*, **16**, 640 (1914)) recalculates the rotation frequencies of HCl in a manner somewhat different from that employed by E. von Bahr, and concludes that the agreement is as good as can be expected in view of the unavoidable experimental error in determining the position of the successive sub-maxima.

More recently the fine structure of the short infra-red atomic vibrational bands of HCl, HBr, and HF has been examined by Randall and Imes (*Physical Rev.*, **15**, 152, 1920; *Astrophys. J.*, **50**, 251, 1919). Using a grating greater resolution of the bands has been obtained than was possible hitherto. The "double-headed" band possessed by HCl with its central depression at about 3.46μ has been resolved into 24

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narrow bands—in place of the ν_{12} observed by E. von Bahr—12 bands on each side of the central depression. According to the simple rotational theory these narrow bands or sub-maxima should be symmetrically placed about the central position, but what is actually found is an unsymmetrical grouping. The mid-points of successive sub-maxima are located successively farther and farther toward the long wave end of the spectrum. This indicates that the vibrational frequency is a function of the rotational frequency and that the vibrational frequency is slowed down as the energy stored by rotation increases. Allowance was made by a graphical method for this lack of symmetry and the true central position of the band found by extrapolation. This corresponds to the atomic vibrational frequency completely uninfluenced by molecular rotation. The wave-length is 3.4637μ as against the earlier value 3.474μ . In the case of HBr and HF the central wave-lengths obtained by similar methods are found to be 3.9075μ and 2.5237μ respectively.

Randall and Imes have also found that the quantity $\nu_{n,r}/n$, which should be a constant in view of the relation :

$$\nu_{n,r} = nh/4\pi^2 I,$$

shows a slow diminution in the case of all three gases, just as E. von Bahr had found for the case of HCl. "This is most readily accounted for by assuming that I , the moment of inertia of the molecule, increases with the speed of rotation."

The "harmonic" of the 3.46μ band of HCl, namely that with a wave-length $3.46/2$ or 1.73μ , was also examined. It also was found to consist of a number of sub-maxima, ten at least, distributed unsymmetrically on each side of the central position. The extrapolated centre is found to be at 1.7646μ (*cf.* Schaeffer and Thomas, *Zeitsch. Physik*, **12**, 330, 1923), which is distant 0.033μ from the position it would occupy if it were precisely one half the wave-length or double the frequency of the 3.4637μ band centre. The displacement 0.33μ is towards the long wave side. Kemble (*Physical Rev.*, **15**, 95, 1920) has suggested an explanation of this on the basis of Bohr's theory (Chapter V.). Kemble likewise considers the asymmetry of the grouping of the sub-maxima observed by himself and Brinsmade round the central position and shows that the frequency of vibration of a rotating diatomic molecule decreases with increasing angular velocity of rotation, a consequence of the non-linearity of the law of force. The results obtained by Randall and Imes have been examined in detail by Kratzer (*Zeitsch. fur Physik*, **3**, 289, (1920)) who explains the unsymmetrical nature of the band on a basis very similar to that adopted by Kemble. The treatment of rotations on the basis of Bohr's theory is given in chapter V. (section on Infra-red absorption spectra of gases) and also in Appendix VI.

Perhaps the best argument in favour of the general correctness of the rotational origin attributed to the long infra-red spectrum is the fact that the value of the moment of inertia of a molecule calculated therefrom leads in turn to values for the distance apart of the two atoms

in a diatomic molecule which are in satisfactory agreement with the accepted values.

Since the moment of inertia of a diatomic molecule has already been shown to be given by the expression: $I = l^2 \cdot m_A m_B / (m_A + m_B)$ where m is the mass of an atom and l the distance apart of the atomic centres, it follows that if we know the masses of the two atoms in a diatomic molecule and their distance apart we can calculate I . Alternatively, if I be calculated from the fundamental rotational frequency by means of the expression $\nu_0 = h/4\pi^2 I$, in the case of a diatomic gas, the masses of the atoms of which are known, it is possible to calculate the value of l , which should be comparable with the accepted value for the radius of the molecule. Kratzer has carried out this calculation with the results shown in the following table for the three halogen hydrides examined by Randall and Imes.

Gas.	$I \times 10^{40}$	$\left(\frac{h}{4\pi^2 I} \right) \times 10^{24}$	$l \times 10^8$ cm.
HF	1.325	1.57	0.92
HCl	2.594	1.620	1.265
HBr	3.258	1.646	1.407

It will be observed that the values of l are very much what we would anticipate not only as regards absolute magnitude but also as regards relative position.

Lenz (*Physikal. Zeitsch.*, **21**, 691, 1920) has also applied the rotational expression to the case of the fluorescence (emission) spectrum of iodine vapour, the fluorescence being caused by exposure of the vapour to the single mercury line $5462\text{\AA}$ —observations of Wood (*Phil. Mag.*, **35**, 236, 1918). From the observed frequency differences between two lines of a certain doublet Lenz finds that I is approximately 2×10^{-38} , whence $l = 1.4 \times 10^{-8}$ cm. as the distance of the two iodine atoms apart in the iodine molecule. The values of I for other gaseous molecules are calculated by Schwarzschild (*Sitzungsber. Preuss. Akad.*, p. 567, 1916).

The problem as to whether two gaseous isotopes could be detected in the rotational spectrum has been considered by Loomis (*Astrophys. J.*, **52**, 248, 1920) who points out that the molecule of a compound such as HCl, HBr or HF would be a more favourable case to examine (with the object of detecting the presence of isotopic forms by the suggested method) than an elementary monatomic molecule. Aston has shown that gaseous chlorine is not a single substance but consists of two isotopes, the atomic weight of the chlorine atom in the two cases being 35 and 37 respectively. It follows that the moment of inertia I of an HCl molecule containing Cl = 35 will not be the same as the moment of inertia of an HCl molecule containing Cl = 37, provided the l term—the distance apart of the atomic nuclei—is the same. Ordinary gaseous HCl

may be regarded as a mixture of two such forms. The difference in the moment of inertia should give rise to a slightly different ν_0 where ν_0 is the fundamental rotational frequency. Loomis calculates that the difference should amount to 1 in 1330 in the case of HCl and to 1 in 6478 in the case of HBr. "Examination of the absorption spectrum of HCl, HBr, and HF plotted by Ipes shows that each rotational quantum line in the first harmonic of the HCl spectrum (*i.e.* the complex band having its centre at 1.7646μ) has on the long wave side a satellite of less intensity and separated from it by an average measured interval of 14 Ångström units or 4.5 wave-numbers, which agrees within the probable error of measurement with the calculated value of 4.3 wave-numbers. These satellites are the predicted lines due to the heavier isotope. Fluorine has been shown to be pure (*i.e.* of one form only) with atomic weight 19, and the absorption spectrum of HF accordingly consists of single lines. In the case of HBr the computed separations are smaller than for the harmonic of HCl and the lines of separate isotopes have not yet been resolved."

What appears to be a serious difficulty in connection with the rotational theory of infra-red frequencies is the fact of the absence of the central line of the short infra-red band due to atomic vibration. This point is taken up in Chapter V, in the section dealing with molecular rotations (infra-red absorption spectra of gases) from the standpoint of Bohr's theory, and likewise in Appendix VI.

It is also necessary to emphasise, as has been done by Baly (*Phil. Mag.*, **39**, 565, 1920), that each of the small bands or sub-maxima, such as those shown in fig. 9, are themselves complex, each small band consisting of a number of lines. Sleator's work on water vapour already referred to demonstrates this. This complexity is evidently not accounted for at all by the Bjerrum theory as it stands. It indicates, therefore, a serious limitation in the applicability of the theory. As a way out of the difficulty it might be suggested that during rotation the molecule suffers nutation superimposed on the rotation, such nutation corresponding to vibration frequencies extremely far in the infra-red—further even than those corresponding to rotation—and these when compounded with the rotational-vibrational sub-bands in the short infra-red introduce frequency differences still smaller than those calculated by Bjerrum.

Baly (*loc. cit.*) criticises adversely the rotational theory also on the ground of the inexactness of the calculated rotational frequencies. In place of the rotational theory Baly substitutes a mode of treatment based on three sets of frequencies, namely *molecular*, *intra-molecular*, and *atomic*. Each of these sets is characterised by certain frequencies. Thus the whole series of absorption bands exhibited by SO₂ can be expressed in terms of three fundamental frequencies namely, 2.4531×10^{11} , 8.19×10^{11} , and 1.296×10^{12} . The first of these is found to be characteristic of the atom of oxygen, the other two being characteristic of the atom of sulphur, all three being atomic frequencies. That such values are really characteristic of the atoms is shown by the striking fact

that the same values may be employed in the case of other compounds containing the atom in question. Thus in dealing with the bands exhibited by water vapour in the infra-red, the frequency 2.4531×10^{11} characteristic of the oxygen atom as deduced from the behaviour of SO_2 is found to play an essential part.

In connection with SO_2 Baly points out that the least common multiple of the three frequencies of oxygen and sulphur given above is 2.89299×10^{12} and this number multiplied by 10, 12, 14, 18, 26, and 33 gives the exact central frequencies of *all* the absorption bands which have been observed for sulphur dioxide in the infra-red region between the wave-lengths 12μ and 3μ . Then again, of these absorption bands the one with the central frequency $2.89299 \times 14 \times 10^{12}$ has the greatest intensity and this central frequency (which corresponds to $\lambda = 7.4\mu$) when multiplied by 25 gives the exact central frequency of the less refrangible band in the ultra-violet, *viz.* $\lambda = 296.1\mu\mu$, the central frequency of the more refrangible band not having been observed. The least common multiple of the three atomic frequencies is called by Baly the molecular frequency, such molecular frequency determining, as we have seen, by means of a series of integral multipliers, the central frequencies of the heads of bands in the infra-red region. Each band, however, contains sub-maxima and the position of these are related by means of a series of integral multipliers to the least common multiples of *two* out of the three atomic frequencies, whilst the component lines of each sub-maximum are due to the atomic frequencies themselves. The frequency obtained by taking the least common multiple of any two out of the three atomic frequencies is called the intra-molecular frequency. "Each complete absorption band, therefore, consists of a central or true molecular frequency compounded with intra-molecular frequencies in the central lines of the sub-groups and with atomic frequencies in the component lines of the sub-groups."

This least common multiple principle has been applied with success by Baly to the structure of the two bands in the neighbourhood of 6μ and 3μ exhibited by water vapour. For the details the original paper must be consulted. At the present time the mechanical significance of the characteristic frequencies, atomic, intra-molecular, and molecular, is not clear. Nor has any reason been assigned for the particular choice of the integral multipliers or their physical significance. The accuracy, however, with which the method of treatment permits of even very complex spectra being calculated in detail indicates the validity of the least common multiple principle, and also indicates the close connection there is between the absorption exhibited by a substance in the infra-red with its absorption in other regions of the spectrum.

Finally, yet another alternative to the Bjerrum rotation theory has been proposed by Krüger (*Ann. Physik*, [iv.] **50**, 346; *ib.*, **51**, 450, (1916)), who replaces rotations by *precessional vibrations* of the molecule, the early Rutherford-Bohr structure of the *molecule* (compare Chapter V.) being assumed and gyroscopic properties attributed to it. At suffi-

ciently high temperatures the precessional vibrations are regarded by Kruger as merging into true rotations. There are serious objections to the precessional theory of far infra-red bands. The point is briefly considered in Appendix VI.

Before leaving at this stage the problem of band spectra, certain considerations, due to R. T. Birge (*Astrophys. J.*, **55**, 273, 1922) which deal with band spectra in the ultra-violet as well as in the infra-red may be mentioned. To a certain extent the treatment anticipates that given later (Chap. V.) in which the concept of discontinuous transition from one state to another in the sense of Bohr's theory is applied to band spectra. According to Birge "there is no essential difference in the structure of near infra-red bands such as the halogen acid bands investigated by Imes [*loc. cit.*] and by Colby and Meyer (*Astrophys. J.*, **50**, 251, 1919) and many ordinary bands in the visible and ultra-violet, such as the cyanogen band $3883\text{\AA}$ investigated in great detail." . . . "Each true band consists of one series having two similar branches. The common origin of these two branches is a 'line' of zero intensity and is labelled $m = 0$. From this point the positive branch runs towards the longer wave-lengths and successive lines [*i.e.* sub-maxima] are designated $m = +1, +2, +3$, etc. The negative branch runs in the opposite direction and the lines [sub-band maxima] are designated $m = -1, -2, -3$, etc. Successive lines [sub-bands] are not equally spaced but crowd closer together in one direction until the series presently reaches a turning-point where the separation of successive sub-bands has become zero, and then turns back on itself." [Reference is here being made to what is actually observed in the ultra-violet band such as that of cyanogen; the apparently different behaviour of the short infra-red band of, say, HCl is discussed below.] "This turning-point is what has always been known as the 'head' of a band. Either the positive or negative branch may thus invert. In the former case, illustrated by the $\lambda = 3883$ CN band, the band is said to be degraded towards the violet, while in the latter case, illustrated [partially] by the halogen acid infra-red bands, the band is said to be degraded towards the red."

"The two types of bands, ultra-violet and infra-red, do not appear similar in structure, due mainly to the fact that the infra-red bands have not been followed to the 'head' because of the rapid decrease in intensity of the 'lines'. But this in turn is due merely to the low temperature of the absorbing molecules in the experimental conditions employed." [Note that, in the above, the word "head" is used to denote the turning-point of the sub-maxima; the true head is the missing narrow band which would correspond with the true central position of the whole system of sub-bands which constitute the broad band.] "Theoretically each 'line' of a band series corresponds to a different change of molecular rotation."

"In the case of all visible and ultra-violet bands it has been customary to consider a series as starting at the point at which $\Delta\nu = 0$

[*i.e.* the turning-point in the sub-maxima separations] where a strong head generally appears and the lines are numbered from this point. . . .” At first sight it would appear that a very serious error might have crept in in thus taking the turning-point as the head of the whole band instead of taking the true central position.¹ In ultra-violet bands, however, the turning-point is reached within a small distance from the true central position and the difference is not great. In the case of the infra-red band of, say, HCl, in which the turning-point has not been observed owing to the failure in absorbing power, the turning-point would naturally be considerably separated from the true central position.

The idea that a series has two branches centering at a point other than the head of the band is due to Fortrat (Thesis, Paris, 1914.)

THE MOLECULAR HEAT OF HYDROGEN GAS AT LOW TEMPERATURES.

(*Cf.* A. Eucken, *Sitzungsber. kon. preuss. Akad. Wissenschaft*, p. 141, 1912.)

The molecular heat of hydrogen is of particular interest, because hydrogen is the simplest type of diatomic molecule. The most striking result obtained by Eucken is that at low temperatures hydrogen behaves as a monatomic gas, *i.e.* it exhibits no energy of a rotational kind. The experimental details will be found in the paper referred to. It is sufficient in the present instance to quote certain of the results. Eucken employed different quantities of hydrogen in the calorimeter (internal volume, 39 c.c.s.), and his experiments are sufficiently exact to show that the molecular heat varied with the concentration of the gas. The following table gives the value of the molecular heat observed corresponding to a particular temperature,¹ and the mass of hydrogen employed.—

T Abs	Gram-moles of H ₂	Molecular Heat
273·1	0·0966	4·94
19·4	0·1710	4·39
9·1	0·3550	3·44
9·1	0·1315	3·32
8·2	0·1268	3·30

The data obtained at still lower temperatures are given in the following table.—

¹ The molecular heat values are “instantaneous,” or true molecular heats *at a given temperature*; not mean values over a temperature range.

T Abs.	Gram-moles H ₂ .	Molecular Heat.	Gram-moles H ₂ .	Molecular Heat.	Gram-moles H ₂ .	Molecular Heat.
35	0.1909	3.42	0.1794	—	0.1040	3.20
40		3.28	• "	—	"	3.18
45		3.30	"	3.28	"	3.13
50			"	—	"	3.13
60			"	—	"	3.09
65		3.21	"	—	"	3.14
70		3.26	"	—	"	3.16
80	0.2585	3.29	0.1295	3.23	"	3.20
85		3.34	"	3.27	"	3.32
90		3.42	"	3.31	"	—
100		3.64	"	3.37	"	—
110		3.82	"	3.62	"	—

It will be seen that the lower the concentration of the gas the lower the molecular heat.¹ This effect is taken account of by the thermodynamic relation—

$$\frac{\partial C_p}{\partial T} = \frac{\partial p}{\partial T^2}$$

To make use of this expression Eucken employs a relation of D. Berthelot which connects the molecular heat at any given concentration with that of the substance in the ideal gas state.² In this way Eucken arrives at the following values for the molecular heat of hydrogen in the ideal gas state:—

MOLECULAR HEAT OF HYDROGEN IN THE IDEAL GAS STATE.

T Abs.	Molecular Heat
35	2.98
40	2.98
45	3.00
50	3.01
60	2.99
65	3.04
70	3.10
80	3.14
85	3.21
90	3.26
100	3.42
110	3.62
196.5	4.39
273.1	4.84

These values show that the molecular heat of hydrogen falls rapidly with a fall in temperature, finally (at about 60° abs.) attaining a value 2.98, identical with that of a monatomic gas. Eucken finds that the molecular heat curve shows even a more rapid fall than that given by

¹ This is not true universally for hydrogen, *i.e.* at very high pressures there is a tendency for C_v to diminish.

² Berthelot's expression involves the critical temperature and critical pressure of the gas. •

the Einstein formula for monatomic solids. In general the molecular heat of a diatomic gas such as hydrogen is due to three types of energy, namely energy of translation, of atomic vibration and of molecular rotation. The first of these gives rise to the term $(3/2)R = 2.98$ in the molecular heat, this term retaining its value (theoretically) at all temperatures. The atomic vibrations as we have seen in the case of diatomic gases generally are of high frequency, *i.e.* short infra-red. On the basis of the quantum theory, therefore, the probability of a contribution from this source to the observed molecular heat will become exceedingly small even before the temperature has attained very low values. This is implied in the formulæ used in connection with the atomic heats of solids where the energy is entirely of the vibratory type. It will be recalled that carbon happens to possess a characteristically high frequency—though even this frequency is distinctly less than that attributed to the atomic vibrations of a diatomic gas molecule—with the result that the atomic heat of carbon is much less than, say, that of copper at room temperature and becomes zero at temperatures well above absolute zero. We have already seen on the equipartition theory that the molecular heat of a diatomic gas should be 7. Even at a temperature as high as 273° abs. the molecular heat of hydrogen is only 4.84, indicating that at this temperature the contribution due to atomic vibration is quite insensible. At 273° , therefore, the molecular heat of hydrogen is due to translation of the molecule together with rotation of the molecule. If we now proceed to lower the temperature it follows on the basis of the quantum theory that the rotation should contribute less and less to the molecular heat, since the chance of a molecule possessing a single quantum of the rotational type becomes less. That the molecular rotational term $\nu = 10^{12}$ to 10^{13} persists at temperatures at which the atomic vibrational term $\nu = 10^{14}$ has already become insensible is due to the fact that the quantum $h\nu$ of rotation is considerably smaller than that of vibration, so that the chance of possession of a rotational quantum is greater at a given temperature. The chance of possession of a quantum of any size diminishes, however, as the temperature falls, so that at sufficiently low temperatures even the rotational term will vanish and we will be left with the translational term $(3/2)R$ as constituting the whole molecular heat of the gas, as observed by Eucken.

In the case of hydrogen that part of the observed molecular heat (from 273° down to 35° abs.) which is due to the existence of rotational energy may be easily obtained by subtracting 2.98 from Eucken's values. In this way the following values for C_r , the molecular heat term due to rotation, are obtained:—

T, °	35°	45°	65°	80°	90°	100°	110°	196.5°	273.1°
C_r	0.00	0.02	0.06	0.16	0.28	0.44	0.64	1.31	1.86

The upper limit of C_v is given by assuming equipartition and is therefore R itself, namely 1.985, since rotation of a diatomic molecule involves two degrees of freedom and the energy kinetic only. This value is not yet reached in the case of hydrogen at 273° abs. It is evident from the data that C_v , which is practically zero at very low temperatures, at first slowly rises, then rapidly, and finally, slowly again. This is reminiscent of the atomic heat of solids which we have seen can be accounted for by quantum considerations. As already mentioned, however, the values of C_v rise more rapidly with temperature than can be accounted for on the basis of Einstein's equation or the equation of Nernst and Lindemann. Thus to account for the absence of rotational energy in the neighbourhood of 35° abs. it would be necessary to assume (on the basis of either of the equations referred to) that the single frequency adopted was of the same order of magnitude as that possessed by carbon in respect of atomic vibrations, *viz.* ca. 10^{13} . At higher temperatures, however, the observed rotational term is much greater than that which would be accounted for on the basis of a frequency as large as this.

Although it is impossible at the present time to account quantitatively for Eucken's results, the data quoted illustrate a point to which attention may be drawn. In the case of a rotating molecule the energy of rotation is given by $\frac{1}{2} \cdot I \cdot (2\pi\nu)^2$ where ν is the frequency of rotation and I is the moment of inertia of the diatomic molecule. Since the rotation of a molecule is due to collisions with neighbouring molecules it is evident that in general the smaller the moment of inertia, I , the larger the frequency of rotation. This means in turn that the rotational quantum $h\nu$, for a molecule of very small moment of inertia, is relatively large, and hence the probability that a molecule possesses it is correspondingly decreased. That is, in the case of a molecule possessing a very small moment of inertia the contribution to the molecular heat made by rotation will disappear sooner (*i.e.* at a higher temperature) than it will in the case of a molecule having a larger moment of inertia. This explains why the molecular heat of hydrogen reaches the value 2.98 (due to translation alone) at a higher temperature than that at which, say oxygen, would be expected to reach the same limit; for, owing to the smaller dimensions and lighter atoms in hydrogen, the moment of inertia of hydrogen is less than that of oxygen or indeed of any other diatomic gas. As a matter of fact no one has as yet (1922) observed the molecular heat of any gas other than hydrogen down to temperatures low enough to cause the rotational term entirely to disappear.¹

What has just been said about the significance of the magnitude of the moment of inertia of a molecule in respect of rotational energy has

¹ Thus Bartels and Eucken have shown recently (*Zeitsch. physik. Chem.*, **98**, 70 (1921)) that the molecular heat of nitrogen at constant volume at a temperature as low as 92° abs. is approximately 4.96 for the gas in the ideal gaseous state. On subtracting the translational term 2.98 from the above value we obtain 1.98 as the contribution due to molecular rotations. This is practically identical with the value of R itself, namely 1.985, which represents the upper limit or equipartitional value of the rotational term. In other words, the frequency of rotation of the nitrogen

a direct bearing on *monatomic gases*. These are characterised by possessing, over the range of temperature so far investigated, energy of translation alone. The possible rotation contributes nothing to the molecular heat. This is due to the extremely small moment of inertia, much smaller than that of hydrogen. The corresponding frequency of rotation in the case of a monatomic molecule is very large, so that it would only be at extremely high temperatures that the chance of possession of a quantum by a molecule would become great enough to contribute a sensible amount to the molecular heat in virtue of rotation. The smallness of the inertia in monatomic molecules is in complete agreement with the view of atomic structure put forward by Rutherford and Bohr (Chap. V.) according to whom almost the entire mass of the atom is concentrated on a nucleus of almost infinitesimal dimensions at the atomic centre.

THE "DEGRADATION THEORY" OF GASES.

(Cf. Nernst, *Conseil Solvay*, 1911; *Zeitsch. Elektrochem.*, **20**, 357, 1914; *ibid.*, **22**, 185, 1916; *Verh. Deutsch. phys. Ges.*, p. 99, 1916. Nernst, "Grundlagen des neuen Warmesatzes" (Knapp), 1918.)

Eucken (*Ber. Deutsch. phys. Ges.*, **18**, 4, 1916) has measured the molecular heats of hydrogen and helium at high pressures and at very low temperatures and has found that the molecular heat falls even below the value $\frac{3}{2}R$ (2.98). The following are the data in the case of hydrogen:—

$T = 29.6^\circ$	24.0°	21.2°	18.6°
$C_v = 3.20$	3.02	2.78	2.70

The first of these values, namely 3.20, when recalculated by the aid of

Berthelot's equation, corresponds approximately to the value 2.98 for the ideal gas state. The remaining values correspond therefore to molecular heats even less than that of a perfect monatomic gas, where the whole of the energy is kinetic energy of translation. Further, the greater the degree of compression the lower the value of C_v . This is represented in the accompanying diagram in which v_1 is greater than v_2 .

C_v |

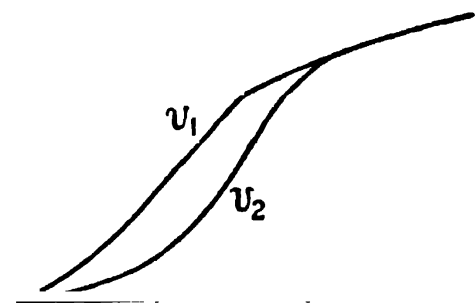


FIG. 10.

molecule is so much smaller than that of hydrogen that even at 92° abs. the quantum treatment of the rotation merges into the classical treatment. To obtain evidence of quantisation of rotations in the case of nitrogen it would be necessary to make observations at temperatures much lower than 92° abs.

This remarkable behaviour is discussed by Nernst, who regards this degradation of the ideal gaseous state as due to the substitution of circular rotational motion of the molecules around fixed points at very low temperatures in place of free translation. It is assumed, in fact, that at exceedingly low temperatures a gas, even a dilute one—though its dilution must be finite—behaves somewhat like a solid. There is a distinction, however. In the case of a solid we must conclude that even under zero pressure the small units composing the material occupy certain fixed positions with respect to one another defined by the fact that compression has to act against forces of repulsion whilst expansion is opposed by forces of attraction. In the case of a gas in the degraded state repulsive forces *alone* are postulated, so that, even in this state—which only has significance for very low temperatures—the gas occupies completely the containing vessel as it does at ordinary temperatures.¹

Nernst further assumes that each molecule rotates² in as wide a circle as possible without interfering with the motion of its neighbour. That is, if V is the volume occupied by one gram-molecule of gas in the degraded state and r is the radius of rotation of a molecule, we can write as a first approximation—

$$N\frac{4}{3}\pi r^3 = V,$$

where N is the Avogadro constant. A more correct expression is obtained if we make allowance for the fact that the circular rotational orbits are orientated in a completely random manner. For the sake of simplicity suppose that one mole of a gas is in a cube the length of one side of which is $V^{1/3}$. Then, making the usual approximate assumption that the molecules may be divided into three groups we obtain—

$$\begin{aligned}\frac{1}{3}N\frac{4}{3}\pi r^3 &= V^{2/3} \\ &= \frac{3V^{2/3}}{\pi N^{2/3}}.\end{aligned}$$

Consider the case of a single molecule rotating with velocity v in an orbit of radius r . It follows that the frequency ν of rotation is given by—

$$\nu = v/2\pi r.$$

Further, since the energy is kinetic only and there are three degrees of freedom we can write the quantum relation—

$$\frac{3}{2}h\nu = \frac{1}{2}mv^2$$

where m is the mass of a molecule.

¹ It will be observed that the deviations from the ordinary gaseous behaviour considered here have nothing to do with the deviations from the perfect gas law exhibited by gases at higher temperatures (taken account of by the various equations of state), for in the case considered the gas may be very dilute (though not infinitely so) and yet exhibit degradation.

² It will be observed that the word rotation is here used in a different sense from the “true” rotation or spin of a molecule round an axis passing through the molecule which is the kind of motion envisaged in the so-called “rotational spectra,” etc.

Whence

$$\nu = 3h/4\pi^2 r^2 m$$

and since

$$r^2 = \frac{3}{\pi} \cdot \frac{V^{2/3}}{N^{2/3}}$$

we obtain—

$$\nu = hN^{2/3}/4\pi m V^{2/3} \quad (1)$$

It is evident, therefore, that ν is a function of V , decreasing as V increases. For a gas of unit molecular weight and occupying 22.4 litres, ν would have the value 10^9 . (For true molecular rotations (Bjerrum) the corresponding quantity is of the order 10^{12} .)

Turning now to the energy E of a gas at very low temperatures, instead of writing $E = \frac{3}{2}RT$ in which energy is due to free translation we must write for a gas in the degraded state in which the energy is due to “rotation”—

$$E = \frac{3}{2}R \cdot \frac{\beta_0 \nu}{e^{\beta_0 \nu/T} - 1} \quad (2)$$

This important relation requires that the molecular heat shall fall below the value 2.98, and, in fact, become zero as the absolute zero of temperature is approached. Owing to the small value of ν , it is only at very low temperatures that equation (2) differs sensibly from the value $\frac{3}{2}RT$. It is also to be remembered that ν itself is a function of volume so that E depends on T and V simultaneously.

(NOTE.—Even in the case of a diatomic gas the work of Eucken has shown that at low temperatures (though still at temperatures above the degradation region) the molecular heat becomes identical with that of a monatomic gas, because the true molecular rotations (or spin) which accompanied the translational motion and were in fact due to collisions have become vanishingly small. At still lower temperatures the degradation sets in. That is, “rotations” of the kind envisaged in degradation make their appearance. In the latter case they are not caused by collisions but are due to the transformations of free translational energy, presumably *per se*, into “rotational” energy. It is evident that the frequency term which characterises the true molecular rotations which exist at higher temperatures must be much greater than the corresponding term required to account for the degraded state. Such considerations as these indicate the high degree of speculativeness which characterises the whole concept of degradation.)

The chief importance of the concept of the degradation theory of the gaseous state lies in the possibility which it affords of applying the Nernst heat theorem *directly* to gases. Nernst assumes, in fact, that on the basis of the concept of degradation it is legitimate to write for a gas of finite density—

$$\left. \begin{array}{l} \lim (dp/dT) \text{ const. } \nu = 0 \\ \lim dA/dT = 0 \\ \lim dU/dT = 0 \end{array} \right\} \text{for } T = 0.$$

or
and

Nernst has thus succeeded in calculating the integration constant for a gaseous process by an entirely new method. This is discussed in Chapter IX. For the present we shall assume the applicability of Nernst's heat theorem to the degraded gaseous state in order to obtain an expression for the pressure which would be exerted by a gas in this condition.

For this purpose let us consider a gas in the degraded state and denote its total energy by U and its free energy by A . A is essentially potential energy. Since the U term as here employed increases with rise in temperature, it follows that A will diminish as the temperature rises. At absolute zero A and U are identical by the second law, *i.e.* $A_0 = U_0$. On the basis of the *second* formulation of the quantum theory the total energy of an oscillator possessing three degrees of freedom is $\frac{3}{2}h\nu$ at abs. zero and for N such oscillators (where N is the Avogadro constant) we can write—

$$U_0 = \frac{3}{2}N h \nu$$

and for any temperature above zero—

$$U = \frac{3}{2}N h \nu + E$$

where E is defined by equation (2).

Applying the Nernst heat theorem we can also write for A —

$$A = \frac{3}{2}N h \nu - T \int_0^T \frac{E}{T^2} dT \quad . \quad . \quad . \quad (3)$$

Now,
$$T \int_0^T \frac{E}{T^2} dT = \frac{3}{2}RT \log (e^{\beta_0 h \nu / T} - 1) - \frac{3}{2}N h \nu.$$

Substituting this in equation (3) above we find—

$$A = \frac{3}{2}RT \log (e^{\beta_0 h \nu / T} - 1).$$

But, in general, at constant temperature

$$p dV = dA$$

or

$$p = \frac{\partial A}{\partial V}$$

Differentiating equation (3) with respect to V , keeping T constant, we obtain—

$$p = - \frac{3}{2}R \cdot \frac{\beta_0 e^{\beta_0 h \nu / T}}{e^{\beta_0 h \nu / T} - 1} \cdot \frac{\partial \nu}{\partial V}.$$

From equation (1) we obtain the value of $\frac{\partial \nu}{\partial V}$ and so find as our final expression for the pressure of a gas in the degraded state—

$$p = \frac{R}{V} \cdot \frac{\beta_0 h \nu}{e^{\beta_0 h \nu / T} - 1} \quad . \quad . \quad . \quad (4)$$

It is to be remembered that ν is a function of V , diminishing as V increases. Consequently equation (4) becomes $p = \frac{RT}{V}$ when V or T is sufficiently large. At absolute zero itself, and for a small range above this, the pressure is given by—

$$p_0 = \frac{h^2 N^{2/3}}{4\pi m V^{2/3}} \quad (5)$$

As already mentioned, Nernst assumes that in the degraded state a gas is characterised by forces of repulsion between the molecules. It is of interest to attempt to determine the law of repulsion which obtains under these conditions. This problem is considered by Nernst (*Sitzungsber. preuss. Akad.*, p. 118, 1919) in the following manner.

In the first place, Nernst points out that factors such as 4π (which occurs in equation (5) for example) are relatively uncertain, the theoretical considerations not having attained this degree of precision.

As regards the structure to be assumed for the degraded state the simplest is that the molecules are placed at the corners of cubes. If we denote the distance between two molecules by r we have—

$$V = Nr^3.$$

If the mass of gas expands by dV at $T = 0$ the external work done is—

$$p_0 dV = p_0 N 3r^2 dr \quad (6)$$

This work may be attributed to the forces of repulsion consequent upon increasing r by dr . That is,

$$p_0 dV = dr \Sigma K \quad (7)$$

where ΣK refers to summation over all the molecules. From (5), (6), and (7) it follows that—

$$\Sigma K = \frac{3}{4\pi} \frac{h^2 N}{mr^3} \quad (8)$$

This equation requires that between any pair of molecules the repulsive force k_0 shall be given by—

$$k_0 = A/mr^3 \quad (9)$$

That is, the force of repulsion varies as the inverse cube of the distance. We meet, however, with a difficulty if we assume that this law holds between all the molecules as distinct from neighbouring pairs. If the law applied to the effect of all the molecules upon any one of them it would follow that the pressure caused by the repulsive forces would depend, as Nernst shows (*loc. cit.*), not only on the density of the gas but also upon its degree of expansion. The pressure must depend, however, only on the density and to obtain this condition it is necessary to assume that the repulsions considered operate only *between neighbouring molecules* and do not extend beyond these limits. This suggests at once that the

repulsive force dealt with is analogous to chemical force, say between two atoms; in other words, it is of the nature of a valency force directed between two individuals and not extending beyond them. We may speak therefore of "lines" of repulsive force between neighbouring molecules in the degraded state. The cubical formation assumed for the distribution of the molecules in space requires that there should be $6N$ lines of repulsive force if 6 lines emanate from any individual molecule. Since, however, we are here counting the lines twice over the total number of such lines is $3N$. Hence equation (8) becomes—

$$\Sigma K = 3Nk_0 = \frac{3}{4\pi} \frac{h^2 N}{mr^3}$$

whence

$$k_0 = \frac{h^2}{4\pi m} \quad (10)$$

as the law of repulsion between neighbouring molecules in the degraded state.

It is of interest to see how this law compares, as regards magnitude, with the law of gravitation on the one hand and Coulomb's law on the other. Taking the case of two particles, each carrying one electronic charge and each having the mass of a hydrogen atom, the particles being assumed to be 1 cm. apart, the laws mentioned give rise to the following forces:

$$\begin{aligned} \text{Electrostatic repulsion} &= 0.220 \times 10^{-18} \text{ dynes} \\ \text{Gravitational attraction} &= 0.177 \times 10^{-54} \text{ dynes} \\ \text{Repulsion given by (10)} &= \frac{(6.55 \times 10^{-27})^2}{4\pi \times 1.63 \times 10^{-24}} \\ &= 0.209 \times 10^{-11} \text{ dynes.} \end{aligned}$$

It will be observed that equation (10) leads to a magnitude which is great compared with gravitation but small compared with electrostatic repulsion. If we take the case in which the atoms of hydrogen are separated not by 1 cm. but by the distance 10^{-5} cm. which separates them in the hydrogen molecule the repulsive force given by equation (10) is about one thousandth of the electrostatic force which would exist between two electronic charges separated by this distance. The force though small is therefore not negligible.

The next point is whether a force such as that given by equation (10) could enter into any of the quantities considered in the kinetic theory of gases involving forces of repulsion, notably the mean free path of a molecule with the related phenomena of viscosity, diffusion and heat conduction.

Nernst has considered in this manner the problem of viscosity, making use of the simplifying assumption that all the molecules possess the same kinetic energy $\frac{1}{2}mu^2$. Since this may be regarded as made up of three equal terms in respect of the three space co-ordinates it follows that at a collision occurring along one of these axes the kinetic energy term involved is $\frac{1}{6}mu^2$ for each molecule. The expression of Clausius

for the viscosity η of a gas (which is based on the same assumption that the molecules all possess the same kinetic energy) is

$$\eta = mu/4\pi\sigma^2 \quad (11)$$

where σ is the distance to which two molecules approach in a collision. Naturally on the basis of equation (10) the σ term is not a constant. Its value in any case may be obtained by assuming that the kinetic energy falls to zero at the moment of closest approximation of the two molecules, the kinetic energy being just overcome at this point by the force of repulsion. We have then,

$$2 \times \frac{1}{2}mu^2 = - \int_{\sigma}^{\infty} \frac{h^2}{4\pi m r^3} dr = \frac{h^2}{8\pi m} \cdot \frac{1}{\sigma^2} \quad (12)$$

In this expression it is assumed that at a collision only one of the six repulsive forces is involved; if all six are involved the right hand side becomes $\frac{3h^2}{4\pi m} \cdot \frac{1}{\sigma^2}$. Combining either form of equation (12) with (11) we obtain:—

$$\left\{ \begin{array}{l} \eta = \frac{2}{3} \frac{m^3 u^3}{h^2} \quad (13a) \\ \text{or } \eta = \frac{1}{6} \frac{m^3 u^3}{h^2} \quad (13b) \end{array} \right.$$

That is, the viscosity should be calculable from the molecular weight, the molecular velocity and Planck's constant.

Before attempting to test the applicability of equation (13a) or (13b) it is necessary to point out that equation (10) is based on considerations for which T is in the neighbourhood of zero. In testing the viscosity relation we must restrict ourselves therefore to low temperatures. A low temperature means that the kinetic energy term is small and consequently the intensity of a collision is small, that is, the two molecules do not interpenetrate, or, in other words, σ does not sink below a certain limit. From another point of view we would expect that equation (13) could not apply if the collision involves a value of σ at which the electrostatic forces of repulsion due to the close approximation of rotating electrons in the two molecules becomes the really significant term. It is known that in the case of hydrogen the range of such forces is about 2×10^{-8} cm. Hence it is only justifiable to apply equation (13) to cases for which the σ term is greater than 2×10^{-8} .

From equation (12) it follows that:

$$= \frac{h}{mu} \sqrt{\frac{3}{8\pi}}$$

Applying this to the case of hydrogen at $T = 273$ it follows that $\sigma = 0.38 \times 10^{-8}$; at $T = 21$, $\sigma = 1.35 \times 10^{-8}$. These values are obtained on the basis of a single valency repulsive force operating. If six

such forces operate, then, at $T = 21$, $\sigma = 3.3 \times 10^{-8}$. We may conclude therefore that in the case of hydrogen at temperatures of the order 20° abs. we have a condition to which the viscosity relation may be applied approximately.

It follows from equation (13) that the viscosity should vary as the cube of the average velocity of the molecules, and therefore as $T^{1.5}$. This should hold good at low temperatures. The following table contains the values of the viscosity of hydrogen at various temperatures and also the value of α obtained from the relation

$$\frac{\eta_1}{\eta_2} = \left(\frac{T_1}{T_2} \right)^{1.5}$$

The value obtained for α from this expression will refer to the geometric mean of the two temperatures chosen.

T (abs.) = 273.15	194.6	81.6	21
$\eta \times 10^7 = 50$	670	374	99
$\alpha =$	0.70	0.67	0.98

It will be observed that α remains fairly constant down to 81.6° and then rises so that at a temperature of about 40° its value is 0.98. Hence at 21° it will approximately reach the value 1.5 as required by equation (13). We have seen, however, that the application of (13) is only justified at this temperature provided all six repulsive valencies function. Hence equation (13b) is to be preferred to (13a).

Brillouin had already shown on the basis of Maxwellian distribution of velocities that if the repulsive force between two molecules be $1/r^n$ then

$$\frac{\eta_1}{\eta_2} = \left(\frac{T_1}{T_2} \right)^{1+\frac{6}{n}}$$

From room temperature down to 80° abs. this expression gives a constant value for n , namely 10, identical with the law of repulsion found by Born and Landé for crystal lattices (*cf.* Chap. VIII). Below 80° the value of n diminishes, probably due to the fact that at low temperatures when the molecular velocities are small, the repulsive forces, postulated by Nernst in the degradation theory of gases, first begin to operate and become sensible. As will be seen from the form of equation (13) the greater the mass of the molecule considered the lower must the temperature be at which the equation begins to apply.

We have now to test equation (13b) to see how far it reproduces quantitatively the value of η for hydrogen at 21° abs. On inserting the numerical values we obtain

$$\eta = \frac{1}{9} \cdot \frac{(3.26 \times 10^{-24})^3 (5.10 \times 10^4)^3}{(6.55 \times 10^{-27})^2} = 119 \times 10^{-7}$$

whilst η observed is 110.5×10^{-7} . The agreement is remarkably good.

Equation (13*b*) may also be written in the form—

$$\eta = 0.47(M.T.)^{1.5} \times 10^{-7} \quad (14)$$

where M is the molecular weight.

It would follow from this that at a given temperature the viscosity of different gases should vary as the molecular weight to the power 1.5. At 273° abs. no such relation holds. This equation, however, would only be expected to hold for a very low temperature region, and since the greater the molecular weight the lower the temperature limit, it is evident that for gases of high molecular weight it would be impossible to carry out the necessary measurements. A comparison may be made, however, in the case of hydrogen and of helium. At $T = 21^\circ$ $\eta_{\text{He}}/\eta_{\text{H}_2} = 3.2$ to 3.8 (according to the experimental data employed) whilst $(M_{\text{He}}/M_{\text{H}_2})^{1.5} = 2.83$. The agreement is only moderate.

As already mentioned the degradation theory is again considered in Chapter IX. in connection with the calculation of the chemical constant of a gas. Attention will there be drawn to the considerations of Lindemann which constitute an adverse criticism of the theory of degradation.

CHAPTER V.

Atomic and molecular structure—Distribution of electrons in atoms—Structure of the atom from the standpoint of the quantum theory—the Rutherford-Bohr atom-model—High frequency spectra of the elements—Moseley's relation—Infra-red absorption spectra of gases—Parson's magneton—The Lewis-Langmuir atom-model—The Whittaker-Ewing magnetic model.

The Rutherford Atom-model.

(Rutherford, *Phil. Mag.*, [vi.], **21**, 669 (1911).)

THE underlying idea in this atom-model is that the atom consists of a central charge, concentrated on a nucleus, which is surrounded by an "atmosphere" of electrons, rotating in certain orbits. Practically the whole mass of the atom is to be ascribed to the nucleus. The number of "atmosphere" electrons is not large. The dimensions of the nucleus are considerably smaller than the dimensions of the atom as a whole. Rutherford estimates the diameter of the nucleus to be of the order 10^{-12} cm., whilst the diameter of the atom as a whole is of the order 10^{-8} cm. The nucleus¹ itself possesses a structure about which, however, nothing is known. It, the nucleus, contains probably quite a large number of electrons, but these are bound firmly, except in the case of radioactive materials which are capable of expelling one of these bound electrons in the form of β -rays. The outermost ring of the "atmosphere" electrons contains those which give the property of valency to the atom. The innermost electrons of the atmosphere are the source of X-rays, the shortest wave-length which the atom is capable of emitting. The necessary disturbance of the innermost electron is brought about by collision with a β -ray (cathode ray) which jerks the innermost electron out; on its return journey to the innermost ring it

¹ It may be recalled that on the basis of electromagnetic theory the electromagnetic mass of an electric charge distributed uniformly over a sphere is inversely proportional to the radius of the sphere. The mass of the nucleus of the hydrogen atom is 1835 times that of the electron. Hence on the above basis, the radius of the hydrogen nucleus should be $\frac{1}{1835}$ of that of an electron. Although this is difficult to accept, so little is known about the nucleus at the present time that we must regard it as not impossible. If true, it would follow that the electrons must be compressible or can interpenetrate one another, a view which is in agreement with that suggested by Nicholson (*Proc. Phys. Soc. Lond.*, **30**, 1, 1917), namely that an electron does not possess any definite size, but is to be regarded as a strain in the ether. This would permit of interpenetration. The dimensions usually assigned to the electron are 10^{-12} to 10^{-13} cm. Compton, on the other hand (*Phys. Rev.*, **14**, 247, 1919), regards the electron as a *ring* of electricity having a radius 2×10^{-10} cm.—cf. the atom model of Parsons considered later in this chapter.

causes the emission of the extremely short waves which we call X-rays. Rutherford was led to this planetary view of the atom in order to explain the scattering of α and β particles. When such particles pass very close to the centre of an atom they are violently deflected, an effect which could be produced by a nucleus of the kind referred to. The angle of scattering has been measured by Geiger and Marsden in the case of α -rays, and by Crowther in the case of β -rays. The outer "atmosphere" of electrons rotating in rings do not appreciably affect the direction of the motion of an α particle travelling through the atom. It is only when the α particle comes into close contact with the nucleus that its path is abruptly altered, the path becoming hyperbolic.

Bohr's Application of the Quantum Theory to the Rutherford Atom-model.

(Bohr, *Phil. Mag.*, [vi.], **26**, 1, 476, 857 (1913); *ibid.*, **27**, 506 (1914); **30**, 394 (1915)) *The Theory of Spectra and Atomic Constitution*, 3 essays (Cambridge University Press).

Note.—In the following account the mode of treatment first employed by Bohr in 1913 has been followed in general. This involves certain postulates (which appear to be almost entirely arbitrary) from which a number of relations are deduced, notably the expression for the Balmer series in the emission spectrum of hydrogen. As a result of later work Bohr's theory has been recast, and it is now usual to begin by combining Balmer's empirical expression with the concept of stationary states and so lead to the postulate represented by equation (1). This mode of development is clearly and logically given in N. Campbell's "Series Spectra" (a supplementary chapter to the same author's *Modern Electrical Theory*).

Bohr first of all points out that the Rutherford atom-model, which has just been referred to, suffers from the serious drawback that the system of "atmosphere" electrons is unstable, that is, unstable from the standpoint of classical electro-dynamics. If, however, we introduce quantum mechanics, the instability may no longer exist from the theoretical point of view. The problem of atomic structure affords therefore a further instance of the necessity of introducing some new concept, such as that of Planck, into electro-dynamics in order to account for the observed facts. Bohr first attempts to apply the quantum theory to the process whereby a free electron—such for example as exists in a vacuum tube when a discharge is passed—may be conceived of as attaching itself to a positively charged nucleus. It will be shown that it is possible from the point of view taken to account, in a simple way, for the Balmer law of line spectra of hydrogen and helium, and possibly the theory will eventually be capable of dealing with the spectra of more complicated atomic structures.

According to Rutherford, the hydrogen atom consists of a nucleus with a single electron describing a closed orbit around it. The first assumption is that the mass of the electron is negligible compared with the mass of the nucleus, and that the velocity of the electron is small compared with that of light. Bohr considers that whilst the electron is rotating in this orbit or stationary state it is neither radiating nor absorbing energy.

Such rotation represents an equilibrium condition of the system as a whole. The production of spectra must be due therefore to some kind of departure from an equilibrium state. In general Bohr considers the possibility of a series of such stationary states corresponding to electron orbits of different radius, and *emission or absorption of radiation is due to the electron passing from one stationary or equilibrium state to another*. The quantum idea is introduced in the further hypothesis that during the passage of the electron from one equilibrium state to another, homogeneous radiation of a certain frequency ν is emitted or absorbed, the amount of radiant energy so emitted or absorbed being $h\nu$, where h is Planck's constant. It will be realised at once how very different these considerations are from those based on classical electrodynamics. On the classical view a charged particle rotating steadily in a closed orbit is giving off radiation continuously, and in so doing its orbit gradually becomes smaller so that the electron would finally drop into the nucleus. Furthermore, with the alteration in orbit the wave-length of the light emitted would gradually change, a conclusion which is opposed to direct observation, for spectra are clearly characteristic and unchangeable properties of an atom. Bohr assumes that no radiation at all is given out when the electron is rotating in an orbit.

Let us consider the hydrogen atom, one in which there is a single nucleus carrying unit positive charge, with a single electron revolving around it in a state of equilibrium, the electron traversing a circular orbit with a frequency of revolution ω (number of revolutions per second), the radius of the orbit being a . The work which must be done by an external agent, *i.e.* the amount of energy which must be contributed to the system and be absorbed by it, in order to remove the electron to an infinitely great distance (*i.e.* to dissociate the atom completely into a positively charged nucleus and a free electron) is denoted by W (energy units). The work done by the system itself in this operation is then $-W$, since the force of attraction between nucleus and electron opposes the motion of withdrawal. That is, $-W$ is equal to the sum of the kinetic and potential energies which the electron and nucleus possess in the state of equilibrium referred to. It will be shown later that W , the work required to eject the electron, is numerically equal to the kinetic energy of the revolving electron taken over a complete revolution. The act of removal of the electron necessitates the absorption of radiant energy, *i.e.* it corresponds to an absorption band in the spectrum.

Now let us consider the reverse process, namely, the act of binding a free electron to the nucleus. At the beginning the electron may be regarded as possessing no sensible velocity with respect to the nucleus, *i.e.* its frequency of revolution is zero relatively to the nucleus. The electron, after interaction has taken place, settles down to a stationary orbit—the word stationary refers to the orbit, the electron itself is in rapid rotation round the orbit. The initial free state of the electron represents the extreme limit of a series of stationary states through which the electron is capable of passing. The other limit is given by the

smallest value of $2a$ or the greatest value of ω which necessitates the maximum value of W .

The passage of the electron from the free state (*i.e.* free with respect to the nucleus) to a state of equilibrium which represents the maximum stability of the atomic system (*i.e.* the innermost orbit) is only a special and extreme case of the transition of an electron from any orbit to any other. During the transition from any orbit to another Bohr assumes that homogeneous radiation of a certain frequency is either emitted or absorbed; emitted if the electron has moved inwards towards the nucleus, absorbed if it has moved outwards. This concept is quantised by asserting that the amount of radiation emitted, say, is exactly $h\nu$ where ν is the frequency of the radiation. If we denote by ν the frequency of the radiation emitted in the passage of the electron from the free state to the innermost orbit, the work W which would have to be done to reverse the process is given by—

$$W = h\nu.$$

It is evident that there should be some relation (involving h) between the quantity W and the frequency of revolution ω of the electron in the orbit in which the electron eventually finds itself. (ω and ν are to be clearly distinguished, the first referring to the frequency of revolution of the electron in an orbit, the second to the frequency of the radiation emitted by the passage of the electron from one orbit to another, in the case considered from infinity to the innermost orbit.) Bohr postulates that—

$$W = \tau h \frac{\omega}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where τ is an integer, having any one of the values 1, 2, 3, etc., and indicating by the numerical value attached to it the orbit concerned. Thus for the first or innermost orbit $\tau = 1$, for the second orbit $\tau = 2$, and so on. The value to be attributed to ω likewise varies with the orbit in which the electron is revolving.

We have now to find the relations which exist between the quantities W , ω , and a , for the case of the hydrogen atom, the orbit of the electron being regarded as circular. (Actually, the orbit is probably elliptical, but it is here regarded as circular for the sake of simplicity of treatment. The more general treatment of elliptic orbits is given in Appendix IV.)

Let the points A and B in the diagram represent the nucleus of mass M and the electron of mass m respectively. A and B traverse circular orbits about their common centre of gravity G.

If $\overline{AB} = a$, then, $\overline{BG} = \frac{M}{M+m} \cdot a$, and $\overline{AG} = \frac{m}{M+m} \cdot a$. (These expressions are identical with those already given in the footnote in



Chapter IV. in connection with molecular rotations.) The force holding B in its orbit is assumed to be the ordinary electrostatic inverse square, *viz.*, eE/a^2 , where e is the charge on the electron and E the charge on the nucleus. In the particular case of the hydrogen atom, the magnitudes of e and E are identical. If ω be the frequency of revolution of B around G, the centrifugal force

$$= \frac{mv^2}{BG} = m(2\pi\omega)^2 \cdot BG = \frac{Mm}{M+m} (2\pi\omega)^2 \cdot a.$$

Since the system is in equilibrium the electrical force of attraction must balance the centrifugal force. That is—

$$\frac{eE}{a^2} = \frac{Mm}{M+m} \cdot (2\pi\omega)^2 \cdot a \quad (2)$$

The potential energy of the system consisting of nucleus and electron is $-Ee/a$. The kinetic energy of the same system is given by—

$$(1/2) \cdot M (2\pi\omega)^2 \cdot \overline{AG}^2 + 1/2 \cdot m \cdot (2\pi\omega)^2 \cdot BG^2$$

which is equal to $(1/2) \cdot \frac{Mm}{M+m} \cdot (2\pi\omega)^2 \cdot a^2 = (1/2) \cdot Ee/a$ from equation (2).

$$\begin{aligned} \text{Hence, } -W &= \text{kinetic energy} + \text{potential energy} & \frac{Ee}{a} + \frac{1}{2} \frac{Ee}{a} \\ &= -\frac{1}{2} \frac{Ee}{a} \end{aligned}$$

$$\text{or, } W = \frac{1}{2} \frac{Ee}{a}$$

That is, W , the work required to remove the electron to infinity, is numerically equal to the kinetic energy which the electron had when revolving in its orbit.

Further, we have seen that

$$W = \frac{1}{2} \cdot \tau h \omega.$$

$$\text{Therefore, } \frac{Ee}{a} = \tau h \omega.$$

On squaring this result and substituting it in the expression—

$$W = \frac{1}{2} \cdot \frac{Mm}{M+m} \cdot (2\pi\omega)^2 \cdot a^2$$

we obtain,

$$W = \frac{Mm}{M+m} \cdot \frac{2\pi^2 e^2 E^2}{\tau^2 h^2} \quad (a)$$

from which it follows that—

$$\omega = \frac{Mm}{M+m} \cdot \frac{4\pi^2 e^2 E^2}{\tau^3 h^3} \quad (\beta)$$

and

$$2a = \frac{M+m}{Mm} \cdot \frac{\tau^2 h^2}{2\pi^2 Ee} \quad (\gamma)$$

It is known, however, that the mass of the electron is only $1/1835$ of the mass of the hydrogen nucleus. Neglecting m compared with M , equations (α), (β), and (γ) become—

$$W = \frac{2\pi^2 m e^2 E^2}{\tau^2 h^2} ; \omega = \frac{4\pi^2 m e^2 E^2}{\tau^4 h^3} ; 2a = \frac{\tau^2 h^2}{2\pi^2 m e E} \quad (3)$$

If in these expressions we give τ different values, we get a series of values for W , ω , and a , corresponding to a series of configurations of the system, such configurations being stationary states in which there is no radiation of energy, and in which the electron will remain as long as the system is not disturbed from outside. We see that *the value of W is greatest if τ has its smallest value, viz. unity. This will therefore correspond to the most stable state of the system i.e. it will correspond to the binding of the electron for the removal of which the greatest amount of energy is required.* Substituting in the above expressions $\tau = 1$, and $E = e$ — the charge on a single electron, and introducing the experimental values, viz. $e = 4.7 \times 10^{-10}$, $e/m = 5.31 \times 10^{17}$, $h = 6.5 \times 10^{-27}$, we obtain:—

$$2a = 1.1 \times 10^{-8} \text{ cm} ; \omega = 6.2 \times 10^{15} \text{ per sec.} ; W/e = 1.3 \text{ volt.}$$

We see that these values are of the accepted order of magnitude for the linear dimensions of the atom, the optical frequencies, and the ionisation potential respectively of hydrogen.

It is necessary to emphasise once more precisely how the term W , i.e. the energy which must be supplied to remove the electron to infinity or, what is the same thing, the kinetic energy of the revolving electron, varies from one orbit to another in any atomic system. W depends upon two quantities, namely, the index number τ of the orbit considered and likewise upon the magnitude of ω as shown by equation (1). The quantity ω can take on the values $\omega_1, \omega_2, \omega_3$, etc., according to the orbit specified. At the same time, the kinetic energy of the electron in each of these orbits does *not* correspond to a single hypothetical “semi-quantum” of magnitude $\frac{h\omega_1}{2}, \frac{h\omega_2}{2}$, etc., but contains a different integral number of such “semi-quanta” according to the orbit considered, the integral number being defined by $\tau = 1, 2, 3$, etc.

To make this point clear, consider the hydrogen atom and compare state 1 with state 3.

State 1 is characterised by the quantities W_1, ω_1 , and $\tau = 1$. Hence from equation (3)—

$$W_1 = \frac{2\pi^2 m e^2 E^2}{1^2 h^2} = \frac{h\omega_1}{2}.$$

That is, W_1 is represented by *one* semi-quantum of type ω_1 .

State 3 is characterised by the quantities W_3, ω_3 , and $\tau = 3$,

whence

$$W_3 = \frac{2\pi^2 m e^2 E^2}{3^2 h^2} = \frac{3h\omega_3}{2}.$$

That is, W_3 is represented by *three* semi-quanta of type ω_3 , not by *one* of such semi-quanta. It will be observed that ω varies as $1/\tau^3$, so that $\omega_1 = 27\omega_3$. Hence $W_1/W_3 = \omega_1/3\omega_3 = 9$. At the same time it is to be remembered that the jump of the electron from state 1 to state 3 is accompanied by the absorption of *one* quantum of radiant energy of a frequency ν where ν is given by: $h\nu = W_1 - W_3$.

It is to be clearly borne in mind that the results so far obtained rest on two main hypotheses:—

1. That the dynamical equilibrium of the systems in the stationary states can be discussed by help of the ordinary electrodynamics, whilst the passage of the systems between different stationary states cannot be treated on that basis.

2. That the latter process is followed by the emission of homogeneous radiation, for which the relation between the frequency and the amount of energy emitted is the one given by Planck's theory.

The next problem which Bohr takes up is to show that his theory is capable of accounting for the line spectra of hydrogen.

If we consider the act of binding a free electron to a hydrogen nucleus carrying a positive charge equivalent to the charge on a single electron so that the electron finally rotates in one of the stationary states, the energy radiated out in the formation of this stationary state is given by equation (3), *viz.*—

$$W_\tau = \frac{2\pi^2 mc^4}{h^2 \tau^2}.$$

The amount of energy emitted by the passing of the electron from a state where $\tau = \tau_1$ to a state where τ_2 is consequently—

$$W_{\tau_2} - W_{\tau_1} = \frac{2\pi mc^4}{h^2}$$

The state corresponding to τ_2 is one in which the electron is closer to the nucleus than in the state corresponding to τ_1 ; in short, τ_2 is less than τ_1 , and the linear dimension a of the atom is smaller when $\tau = \tau_2$ than when $\tau = \tau_1$.

If we now suppose that the radiation in question is homogeneous, and that the amount of energy emitted is equal to $h\nu$, we get—

$$W_{\tau_2} - W_{\tau_1} = h\nu$$

and hence

$$\frac{2\pi^2 mc^4}{h^2} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right) = h\nu. \quad (4)$$

This expression gives the frequency of the homogeneous radiation emitted by the gas when the atomic system changes from the stationary state defined by τ_1 to the stationary state defined by τ_2 . If these two states were the only possible ones the gas could only give rise to a single frequency ν . The quantities τ_2 and τ_1 are whole numbers, and a single atom is capable of existing in a corresponding number of stationary

states, so that in general a number of lines will be emitted, as is borne out by experiment. The above expression is capable of accounting for series of lines emitted by incandescent hydrogen. If we put $\tau_2 = 2$ and allow τ_1 to vary, *i.e.* τ_1 can take on the values 3, 4, 5, etc., we get the well-known Balmer series of lines in the hydrogen spectrum. It is noteworthy that to account for the Balmer hydrogen line spectra we have to assume that the electron from an outer orbit passes to the *second* orbit ($\tau_2 = 2$) and not to the first or innermost orbit, which represents maximum stability. If we put $\tau_2 = 3$ and allow τ_1 to vary ($\tau_1 = 4, 5, 6$, etc.), we get the infra-red series of lines observed by Paschen (*Ann. Physik.*, **27**, 565 (1908)).¹ If we put $\tau_2 = 1$ and allow τ_1 to vary we get a series in the extreme ultra-violet, the furthest Lyman region. In the case of elements heavier than hydrogen, *e.g.* platinum, the kind of radiation to be expected on putting $\tau_2 = 1$ corresponds to X-rays. If we put $\tau_2 = 4, 5$, etc., we get series of lines in the extreme infra-red which were not observed at the date at which Bohr formulated his theory. It will be observed that Bohr's theory accounts excellently for those series of lines which have been observed in the case of hydrogen and is even capable of predicting other series in regions not yet examined. Further, the agreement is quantitative as well as qualitative. Putting $e = 4.774 \times 10^{-10}$ electrostatic units; $c/m = 5.31 \times 10^{17}$; and $h = 6.55 \times 10^{-27}$, we get—

$$\frac{2\pi^2 mc^4}{h^3} = 3.28 \times 10^{15},$$

whilst the value obtained experimentally for the factor (the so-called Rydberg constant) outside the bracket in formula (4) is 3.290×10^{15} . The agreement between the observed and calculated value is within the error due to experimental determination of the various quantities involved.

It is usual to express the Rydberg constant in terms of wave-number rather than in frequencies. By wave-number is meant the number of waves occupying a length of 1 cm. in vacuo. Denoting the wave-number by ν^1 where $\nu^1 = 1/\lambda$ (λ being the wave-length), it follows that

$\nu = \frac{c}{\lambda} = c\nu^1$. Hence we can write the Balmer relation thus:—

$$\nu^1 = \frac{2\pi^2 mc^4}{ch^3} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right).$$

The factor outside the bracket (*i.e.* the Rydberg constant) is usually denoted by the symbol N and has the dimensions cm.^{-1} . The constancy

¹ Recent measurements by Brackett (*Nature*, **109**, 209 (1922)) of emission spectra of hydrogen in the short infra-red region have shown the existence of lines at 1.65μ , 1.28μ , 1.09μ , and 0.95μ . "These are the first five members of the Paschen series due to an electron falling into the third ring from the 4th, 5th, 6th, 7th, and 8th rings respectively. The first two of these were observed and accurately measured by Paschen." In addition, Brackett has observed two new lines at 4.05μ and 2.63μ , "which, according to Bohr's theory, may be explained as due to an electron falling from the 5th to the 4th and from the 6th to the 4th rings respectively, forming the first two members of a new series," for which $\tau_2 = 4$.

of this expression is shown in the following table which contains the Balmer series of emission lines exhibited by hydrogen:—

Line.	$\lambda(\text{cm}^{-1})$	$\left(\frac{1}{r_0^2} - \frac{1}{r_1^2}\right)$	$N(\text{cm}^{-1})$
H α . .	15237	$\frac{1}{2^2} - \frac{1}{3^2} = \frac{5}{36}$	109706
H β . .	20570	$\frac{1}{2^2} - \frac{1}{4^2} = \frac{3}{16}$	109707
H γ . .	23038	$\frac{1}{2^2} - \frac{1}{5^2} = \frac{21}{100}$	109705
H δ . .	24379	$\frac{1}{2^2} - \frac{1}{6^2} = \frac{2}{9}$	109706
H ϵ . .	25187	$\frac{1}{2^2} - \frac{1}{7^2} = \frac{45}{196}$	109705

It will be recalled that the Rydberg constant as employed in either of its forms above is based on equation (3), in which the mass of the electron is neglected compared with that of the nucleus. Strictly, the Rydberg constant is not independent of the nature of the gas considered, the exact expression for the Rydberg factor in terms of fre-

quencies being $\frac{Mm}{h^3 \cdot M + m}$. If M refers to the hydrogen nucleus, 4M would refer to the helium nucleus, so that the Rydberg constant for helium would be $\frac{8\pi^2e^4}{h^3} \cdot \frac{4Mm}{4M + m}$.¹ Setting $M/m = 1835$ it may be calculated that the ratio of the Rydberg constant for helium and hydrogen respectively is 4.001635, the value of the ratio observed spectroscopically being 4.001632 (cf. Fowler, *Phil. Trans.*, **214 A**, 258 (1914)). For the case of hydrogen the most exact calculated value of N, expressed in cm^{-1} , is given by Birge (*Physical Rev.*, **17**, 605 (1921) as—

$$N_H = \frac{2\pi^2e^4}{ch^3} \cdot \frac{Mm}{M + m} = 109677.7.$$

On the same basis the most probable value of N for a nucleus of infinite mass is given by—

$$N_\infty = \frac{2\pi^2e^4}{ch^3} \cdot m = 109736.9 \pm 0.2.$$

It may be pointed out that it has not been possible to observe more than twelve lines of the Balmer series in experiments with vacuum tubes whilst thirty-three lines are observed in the spectra of certain celestial bodies. This may likewise be anticipated on the basis of Bohr's theory. According to equation (3) the diameter of the orbit of the

¹ The number 8 in place of 2 occurs because the nuclear charge E on helium is 2e.

electron in the different stationary states is proportional to τ^2 . For $\tau = 12$, the diameter is equal to 1.6×10^{-6} cm., or equal to the mean distance apart of the molecules of a gas at a pressure of about 7 mm. of mercury; for $\tau = 33$ the diameter is equal to 1.2×10^{-5} cm., corresponding to the mean distance apart of the molecules at a pressure of about 0.02 mm. of mercury. According to the theory, the necessary condition for the appearance of a great number of lines is therefore a very small density of the gas, and if this were realised in a vacuum tube the whole mass of gas present would be insufficient to give rise to a measurable intensity of emission. In solar conditions we have large masses of incandescent gas at extreme rarefaction, and hence lines are observed under these conditions which cannot be observed in a vacuum tube.

Bohr next considers the spectrum of helium.

The neutral atom of helium consists, according to Rutherford, of a single positive nucleus of charge $2e$, with two electrons rotating in the same orbit around it. Now, considering the binding of a single electron by a helium nucleus, we get, on putting $E = 2e$, in expression (3)—

$$\frac{8\pi^2 mc^4}{h^3} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right) = \frac{2\pi^2 mc^4}{h^4} \left(\frac{1}{\left(\frac{\tau_2}{2} \right)^2} \right)$$

If we put $\tau_2 = 1$ or $\tau_2 = 2$ in this formula we get series of lines in the extreme ultra-violet. If we put $\tau_2 = 3$ and let τ_1 vary we get a series of lines which includes two of the series observed by Fowler and ascribed by him to hydrogen. If we put $\tau_2 = 4$ we get the series observed by Pickering in the spectrum of ζ Puppis. Every second one of the lines of this series is identical with a line in the Balmer series of the hydrogen spectrum. It is not surprising therefore that these lines from ζ Puppis were ascribed to hydrogen. In Fowler's experiments hydrogen was mixed with helium in the vacuum tube. With helium alone in a vacuum tube the lines given by putting $\tau_2 = 3$ are not shown, as the ionisation of helium is so small. The presence of hydrogen appears to increase the ionisation of helium, due very probably to the fact that a positively charged hydrogen nucleus has a considerable affinity for electrons and consequently causes the helium atom to lose both of its electrons more easily than it would do in the absence of ionised hydrogen. The lines predicted by Bohr's theory refer to the binding of an electron by the helium nucleus which carries a positive double charge. Further, hydrogen atoms are known to be capable of acquiring a negative charge, so that their "catalytic" effect on the helium may be partly due to the affinity of neutral hydrogen atoms for electrons. Bohr explains in this manner a certain set of the lines obtained from a vacuum tube containing hydrogen and helium as due to the presence of the doubly charged helium nuclei combining with electrons. Finally, if we put $\tau_2 = 5, 6$, etc., in the above formula we get series, the strong lines of which are to be expected in the infra-red region.

It has been found experimentally that under high dispersion the

individual lines referred to above are in reality made up of several component lines lying very close together. Sommerfeld (*Ann. physik.* **51**, 125, 1916) has extended Bohr's theory so as to account for this phenomenon. To do this it is necessary, in the first place, to replace the circular orbits by elliptical orbits. Since the energy of an electron depends only on the magnitude of the major axis of its orbit, it follows that in the passage of an electron from one elliptic orbit to another the spectral line emitted—the frequency of which depends upon the change of energy in terms of the equation: $h\nu = W_1 - W_2$ —is the same, whatsoever the eccentricity of the orbits. That is, the same spectral line is emitted in several different ways.

This would be strictly true if the mass of the electron remained constant. But on the classical electromagnetic theory it is known that the mass of an electron varies with its speed, increasing as the speed increases. If we therefore take account of the variation in the mass of the electron resulting from change in speed we conclude that the spectral lines corresponding to orbits of different eccentricity, *i.e.* different speeds, do not coincide exactly. We would expect, therefore, that a broad line instead of a narrow one would be produced, but the broad line would be structureless. If, however, the eccentricities can be quantised, as Sommerfeld assumes, it would follow that the observed line would consist of a number of distinct components. Sommerfeld's treatment is given in more detail in Appendix IV.

We are now in a position to give a physical interpretation of Planck's constant h . Consider equation (1). If we denote the *angular momentum* of an electron rotating round a nucleus by M , it follows that for a circular orbit $\pi M = \frac{T}{\omega}$ where ω is the frequency of revolution and T the kinetic energy of the electron. For a circular orbit we further have $T = W$, as we have already seen. Hence—

$$M = \tau M_0$$

where

$$M_0 = h/2\pi = 1.04 \times$$

If we assume therefore that the orbit of the electron in the stationary state is circular we can say: the angular momentum of the electron round the nucleus in any one of the stationary states of the system is equal to an entire multiple of a universal value M_0 or $h/2\pi$, independent of the charge on the nucleus. The possible importance of the angular momentum in relation to Planck's theory has also been emphasised by Nicholson.

The angular momentum of a particle of mass m travelling with a velocity v cms. per sec. round a circular path of radius a is given by mva . Taking this as applying to an electron rotating in a circular orbit round a nucleus in the most stable configuration of the atom (*i.e.* the electron in the innermost possible orbit) the expression of Bohr requires that the angular momentum shall be $h/2\pi$. Hence—

$$v = \frac{1}{a} \frac{h}{2\pi m} \quad \dots \quad (5)$$

We can only observe a great number of different stationary states by investigating emission and absorption of radiation. In most of the other physical phenomena we deal with atoms in a single state, the state which corresponds to low temperatures. From these considerations we are led to the assumption that the permanent state is the one among the stationary states during the formation of which (from free electron and nucleus) the greatest amount of energy is emitted. According to equation (3) this state corresponds to $\tau = 1$.

As regards the process of absorption of radiation, the existence of Kirchhoff's law (*viz.* that a body absorbs radiation of the same wavelength as it emits), naturally suggests that the same mechanism is to be attributed to absorption as to emission, absorption taking place when an electron passes from an inner orbit to an outer.

Bohr's theory is likewise in agreement with Einstein's expression for the photo-electric effect, *viz.* $T = h\nu - W$, where T is the kinetic energy of the electron ejected under the influence of light of frequency ν , and W is the total amount of energy which would be emitted during the act of binding a free electron to the nucleus of the atom (*cf.* following chapter).

Let us consider somewhat further the permanent state or most stable configuration of the system which consists of a nucleus with a single attendant electron moving in a circular orbit, *i.e.* the hydrogen atom. As regards the stability of this system, two problems arise. First as regards the stability of the electron *in* the plane of the ring or circular orbit, and secondly as regards the stability with respect to displacements *perpendicular* to the plane of the ring. Nicholson has shown that the question of stability is very different in the two cases. While the ring for the latter displacement (displacement perpendicular to the ring) is in general stable, the ring is in no case stable for displacements in the plane of the ring. This conclusion is based upon classical electrodynamics, and Bohr avoids the difficulty by making use of special quantum restrictions. In fact he shows that, (a) the stability of the orbit or ring round which the electron travels is secured through the condition of the universal constancy of the angular momentum $h/2\pi$ of the electron, together with (b) the further condition that the total configuration is that in the formation of which—from a free electron and a nucleus—the amount of energy W emitted, is a maximum; in other words, the stable configuration possesses the least energy. That this assumption leads to the condition for stability may be shown as follows.

Consider an electron rotating round a nucleus and let us assume that the system is in dynamical equilibrium, the radius of the ring being a_0 , the velocity of the electron being v_0 , the kinetic energy being T_0 and the potential energy of the entire system being P_0 . Next consider a configuration of the system in which the electron, under the influence of extraneous forces, rotates with the same angular momentum round the nucleus in a ring of radius a where $a = aa_0$, a being greater than unity.

In this case we have $P = \frac{1}{a} P_0$ (this follows from the definition of

potential energy which is given by $-\epsilon E/a$; also on account of the constancy of angular momentum it follows that $v = \frac{1}{a}v_0$ (compare equation 5), and $T = \frac{1}{a^2}T_0$, for T involves the square of v and therefore the square of a . It follows then that,

$$P + T = \frac{1}{a}P_0 + \frac{1}{a^2}T_0 = (P_0 + T_0) + T_0\left(1 - \frac{1}{a}\right)^2.$$

We see that the total energy ($P + T$) of the new configuration is greater than the $(P_0 + T_0)$ of the original configuration. The system in its original configuration is therefore stable for the displacement considered, for the original configuration corresponds to a maximum value of W , as defined previously, *i.e.* a minimum value for $(P + T)$. It may be repeated that the condition of stability which we have just been considering refers to possible displacements of the electron *in* the plane of the ring.

When the electron in the hydrogen atom is rotating in its most stable (innermost possible) orbit it is usual to speak of the electron as moving in a 1 quantum orbit. On the elementary theory expressed by equation (3) the "quantum number" τ serves to define the number of the orbit. As we shall see later the orbit has really to be defined by two quantum numbers denoted by Bohr by the symbols n and k in the form n_k . For the stable hydrogen atom $n = 1$ and $k = 1$, so that strictly the orbit is designated as a 1_1 orbit. An alternative nomenclature is $(n + n')$ and n . This will be employed later.

Probable Atomic Structure of the Elements on the Basis of Bohr's Later Theory.

Having considered the hydrogen atom system in some detail, we now turn to the next member in the periodic table, namely *helium*.

The neutral helium atom consists of a nucleus carrying a positive charge of magnitude $2e$, with two attendant electrons. We have already pointed out that the binding of a single electron to the free helium nucleus so as to produce a helium atom carrying one positive charge (*i.e.* a helium atom wanting an electron) can be very satisfactorily accounted for (in respect of emission spectra) by means of equation (3), *e.* the system He^+ is closely analogous to the hydrogen atom, the single electron rotating in a circular orbit around the doubly charged nucleus. It follows from equation (3) that for He^+ in its most stable configuration the radius of the orbit is one half that of the orbit of the electron in the hydrogen atom, and W is four times that for the hydrogen atom, *i.e.* the single electron is held with exceedingly great tenacity.

Let us compare this with the case of the *neutral* He atom. If the two electrons were in the same ring—a 1_1 orbit—Bohr shows that the ionisation potential of the neutral atom would be 28.8 volts, whereas

the observed value is close to 25 volts. For this reason alone it is necessary to reject the idea of the two electrons being in the same orbit. To obtain more precise information Bohr approaches the problem of the helium atom (as well as other atoms) from the point of view of the *act of binding the last electron* (in the case of helium the second electron) to the positively charged system represented by the nucleus and the electrons already there (in the case of helium (He^+) only one such electron is already there). Information about this act of binding is afforded by an examination of the spark spectrum of helium. (The significance of arc and spark spectra respectively will be considered later.)

Bohr finally concludes that¹ "in the normal state of the helium atom the two electrons must be assumed to move in *equivalent* r_1 orbits. As a first approximation these may be described as two circular orbits, whose planes make an angle of 120° with one another, in agreement with the conditions which the angular momentum of an atom according to the quantum theory must satisfy. On account of the interaction between the two electrons these planes at the same time turn slowly round the fixed impulse axis of the atom . . ." Some of the foregoing statements merit a somewhat fuller exposition.

It will be observed that we have so far dealt with the cases of hydrogen and helium in their *normal stable* form from the point of view of circular orbits. There is definite evidence, however, in favour of the occurrence of elliptic orbits in the atom as well as the circular orbits originally envisaged by Bohr. Thus the work of Sommerfeld and others has demonstrated that for the simple two-body problems furnished by atomic hydrogen and ionised helium that the more general premise of elliptic (and disturbed elliptic) motion of the electron is necessary to account for the observed fine structure of the individual "lines" of spectra and the resolving effects of electric and magnetic fields on individual lines (*cf.* Appendix IV.). Since *only one electron can occupy any one elliptic locus the possibility of the formation of stable co-planar rings (containing more than one electron) revolving about a nucleus must be abandoned.*

In the application of quantum principles to elliptic orbits, *two* quantum numbers, which we may denote by n and n' replace the single quantum number τ hitherto used to define the stationary state of the system.² The first of these, n , still *defines the constant angular momentum of the electron*, and is termed the *azimuthal quantum number*. The second, n' , is introduced as a consequence of the variation of the

¹ Quotation from Bohr's *Theory of Spectra and Atomic Constitution*.

² It may be noted that use is here made of the *partial* quantum numbers n and n' rather than the *total* quantum numbers used by Bohr in his later papers. The partial quantum numbers are specially suited to a description of the process of quantisation for elliptic motion (*cf.* Appendix IV.) and any subsequent alteration in the nomenclature might lead to confusion. The *total* quantum number n of Bohr corresponds to our $(n + n')$, Bohr's azimuthal quantum number k being our n , so that the stationary state which we denote above by $(n + n')_n$ corresponds to Bohr's n^k orbit.

radius vector in any particular elliptic orbit, and is termed the *radial quantum number*. *Not only is the angular momentum of the system quantised* (as it was in the simpler case of circular orbits) *but so also is the eccentricity of the ellipse*, so that the possible stationary orbits are limited to certain very definite forms. The total energy of the undisturbed system, nucleus-electron, in a stationary state defined by the integers n, n' is

$$-W = \frac{2\pi^2 m e^4 E^2}{h^2(n + n')} \quad (6)$$

This expression for the energy is equivalent to that previously deduced (equation (3)) if $n + n'$ be equated to τ . There is thus essential difference, however, that whereas there is only one circular orbit possible for a given value of the total energy $-W$, a variety of elliptic orbits is available, all of which are distinguished by the same value of the total energy, corresponding to the number of ways in which integral positive values

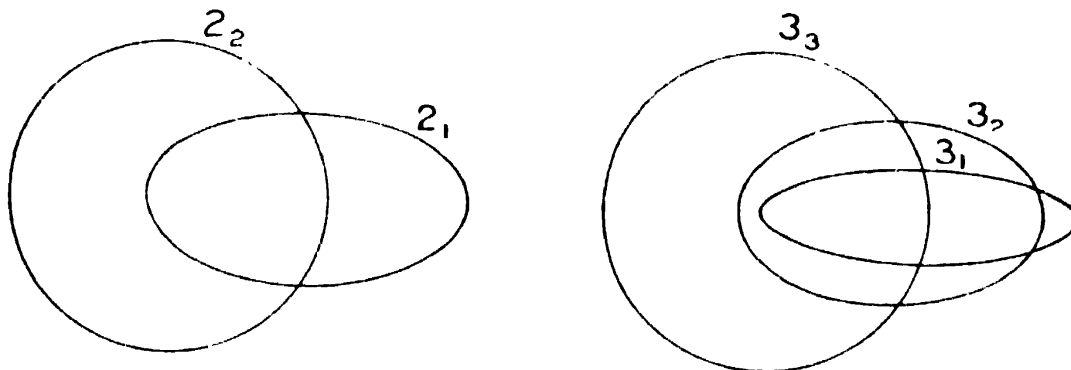


FIG. 11.

can be ascribed to the quantum numbers n and n' , their sum remaining constant. Fig. 11 illustrates the different stationary orbits of the electron, circular and elliptic, for the cases $\tau = n + n' = 2$ and $\tau = n + n' = 3$. A convenient method of distinguishing the different orbits is there employed. The 3_1 orbit corresponds to $n + n' = 3$, $n = 1$, the 2_2 orbit to $n + n' = 2$, $n = 2$, etc.

The H_α line may be generated by transition of the electron from any of the circular or elliptic orbits $3_3, 3_2$ or 3_1 to either the circular or elliptic orbit 2_2 or 2_1 . Obviously, however, the individuality of these orbits cannot be predicted from an examination of the spectral line, unless there be some influence at work, either intrinsic to the system itself and ignored in the mathematical analysis leading up to equation (6), or as a result of external forces, which will exert a specific action on each orbit separately, so that the resulting spectral line will suffer a displacement depending in amount on the actual initial and final orbits of the emitting electron. As already mentioned, such influences are found in the relativistic variation of the mass of the electron with its velocity, and also when the atomic system under observation is placed in a magnetic or electric field (*cf.* Appendix IV.).

A more detailed examination of spectral phenomena combined with recent attempts to correlate the older and newer physics of radiation processes has led to certain very definite, if semi-empirical, principles which define the *intrinsic probabilities* of the various electronic transitions within the atom, and fix the intensity and state of polarisation of the radiation emitted in such transitions. The most comprehensive of these later developments is contained in Bohr's *Principle of Correspondence*.

In his earlier papers, Bohr has drawn attention to the fact that whilst for small values of τ there exists no simple relation between the frequency of a line of the Balmer series and the periodicity of the electron's motion in either of the stationary states involved, yet in the limit when the electron is very far removed from the nucleus and its frequency of revolution is relatively small, the frequency of the radiation emitted in a transition to a neighbouring orbit is identical with the frequency of revolution of the electron or with an harmonic of this frequency. This is what we should expect on the basis of classical electron theory, and there therefore exists in the limit a *correspondence* between the frequency relations of the classical and quantum methods of attack. Bohr now asserts that this same correspondence also obtains for such properties of the radiation as its intensity and state of polarization—properties which have hitherto been left untouched in the development of the quantum theory, but which in terms of classical electrodynamics are very definitely determined by the mode of motion of the electron. The consequences of this far-reaching generalisation or its confirmation in particular cases cannot be given here (*cf.* Appendices IV. and V.) It will be sufficient to state that it has been applied with remarkable success by Bohr and Kramers to the quantum treatment of the Stark and Zeeman effects, where it predicts without ambiguity the particular emission lines which should be observed, their state of polarisation, and (qualitatively at least) their relative intensities.

The dynamic models of Bohr and Sommerfeld have been evolved to interpret the general features of the line spectra of hydrogen and ionised helium; the principle of Correspondence has confirmed and extended the agreement between these models and observation. Bohr has now attempted, by analysis of other optical spectra in terms of the general principles which these simplest cases demand, to elucidate the atomic structures of the more complex elements and correlate these structures with their physical and chemical properties.

Bohr assumes that the normal atom of any element may be regarded as formed by the successive capture and binding of the electrons one by one to the system, each electron occupying that orbit which is most stable with respect to the nucleus and the electrons previously bound. Two types of spectra are known which furnish information regarding the stages of the binding process. For the first of these—the *arc spectrum*—the frequencies of the lines admit of approximate representation in terms of a formula of the type—

$$\nu = R \left\{ (n + n' + \frac{1}{2} a_n)^2 - (m + m' + \frac{1}{2} a_m)^2 \right\} \quad (7)$$

where R is the Rydberg constant of the hydrogen spectrum, and a_n, a_m are constants characteristic of the element under consideration. *The formal resemblance between this and the hydrogen spectrum indicates that arc spectra correspond to the binding of an electron to a system whose effective positive charge is roughly that of the electron itself—that is, the binding of the last electron to form the neutral atom.* On the other hand, the frequencies of the lines of many *spark spectra* are approximately expressed by—

$$= R' \left\{ \frac{1}{(n + n' + b_n)^2} - \frac{1}{(m + m' + b_m)^2} \right\} \quad (8)$$

where the constant R' is just four times the Rydberg constant. *By analogy with the spectrum of ionised helium it follows that the spark spectrum of an element represents the various stages in the capture of the electron last but one in the formation of the neutral atom.*

The arc spectrum of atomic hydrogen affords evidence of the mode by which a single electron is bound to the nucleus, and the most stable orbit of which we have spectroscopic evidence, namely the circular 1_1 orbit, corresponds to the normal structure of this two-body system. Similarly, the final state of the electron in ionised helium (He^+) is also motion in a circular 1_1 orbit. Whilst no spectroscopic data are available which illustrate the formation of doubly charged lithium (Li^{++}), trebly charged beryllium, etc., the conclusion is obvious that the process of *the binding of the first electron in any atom will result in a 1_1 orbit* of the electron round the nucleus.

Further, the binding of the *second* electron to the singly charged helium atom, results, as we have seen, in a second 1_1 orbit. As already mentioned the two orbits are roughly circular (not accurately so on account of the mutual action of the electrons) and their planes make an angle of approximately 120° with each other. A provisional calculation by Bohr and Kramers of the ionisation potential of this model of the helium atom indicates a value in much better agreement with experiment than that computed on the basis of the original electron ring model of Bohr.

As a natural consequence we may regard *the binding of the first two electrons to any nucleus to occur in a manner analogous to that obtaining in the neutral helium atom*, so that in singly ionised lithium (Li^+), doubly ionised beryllium, etc., both electrons occupy 1_1 orbits.

The steps in the capture of a third electron by ionised lithium are illustrated by the arc spectrum of this element. From a consideration of this spectrum, the possibility of the third electron occupying a 1_1 orbit on equal terms with the electrons previously bound is definitely excluded. On the other hand, the arc spectrum and also the selective absorption spectrum of lithium indicate that the firmness of binding of the third electron in its normal state would correspond to motion in a 2_1 orbit. The exact form of this orbit is unknown, but it will obviously approximate to an ellipse, part of which approaches the nucleus to about the same extent as the circular orbits of the first two electrons. The

withdrawal of the electron from the neighbourhood of the internal structure during a part of its revolution (due to the pronounced eccentricity of the 2_1 orbit) may be compared with the readiness with which lithium parts with this, the valency, electron to form the positive ion. In Bohr's own words: "We obtain, therefore, a picture of the formation and structure of the lithium atom which offers a natural explanation of the great difference of the chemical properties of lithium from those of helium and hydrogen. The difference is at once explained by the fact that the firmness by which the last captured electron in its 2_1 orbit in the lithium atom is only about a third of that with which the electron in the hydrogen atom is held, and almost five times smaller than the firmness of the binding of the electrons in the helium atom."

The binding of the first three electrons in succeeding elements will follow the same plan as in the formation of the lithium atom. In the case of beryllium, boron, and carbon we possess no definite spectroscopic data from which the normal orbits of the fourth, fifth and sixth electrons may be predicted, but on general grounds it is very probable that the additional electrons will also move in 2_1 loci. These orbits will be arranged spatially symmetrically with respect to one another, and to the paths of the inner pair of electrons. In carbon, with its valency electrons arranged in four 2_1 orbits we have a structure which exhibits exceptional tetrahedral symmetry. That this symmetry and consequent stability of internal structure may be preserved it is necessary to assume that the additional electrons of the succeeding elements are not bound in 2_1 orbits, but in 2_2 (roughly circular) orbits. The resulting structure of the inert gas neon—two electrons in 1_1 orbits, four electrons in 2_1 orbits and four in 2_2 orbits—will be exceptionally stable, and is considered by Bohr to represent the configuration of the first ten electrons in all the succeeding elements.

Entering the second short series of the periodic table, the final electron to be bound in the formation of the neutral sodium atom will not occupy a 2_2 orbit, since the symmetry of the neon-like substructure would thereby be destroyed, but this electron will probably move in a 3_1 orbit, distinguished by pronounced ellipticity and corresponding to the marked electropositive character of the atom. The further electron captured in the formation of magnesium will occupy a similar orbit. Direct evidence of the existence of this as the normal state is found in the arc spectrum of magnesium. The structure of the aluminium atom is uncertain, as the available spectroscopic data would seem to indicate that the electron last captured occupies a 3_2 orbit. This is, however, in conflict with the general synthetic scheme which has been developed, and certainly the chemical properties of silicon would demand a tetrahedral configuration in this atom in terms of 3_1 orbits analogous to that of carbon. In the case of argon with its 18 electrons in all it would be expected that the configuration should correspond to an arrangement in which the ten innermost electrons move in orbits of the same type as in the neon atom, while the last eight electrons will form a configuration of four 3_1 orbits and four 3_2 orbits, whose symmetrical properties must be

regarded as closely corresponding to the configuration of 2-quantum orbits in the neon atom.

After argon we have the element potassium, the first of the fourth period, possessing 19 electrons in all. As potassium is sharply distinguished from argon in chemical properties and closely resembles the first members (sodium and lithium) of the two previous periods it is necessary to assume that the 19th electron is bound in a new type of orbit which according to Bohr is a 4_1 orbit. At this point, however, a new consideration arises. "With increasing nuclear charge and the consequent *decrease in the difference* between the fields of force inside and outside the region of the orbits of the first 18 bound electrons, the dimensions of those parts of a (necessarily very eccentric) 4_1 orbit which fall outside will approach more and more to the dimensions of a 4-quantum orbit calculated on the assumption that the interaction between the electrons in the atom may be neglected. *With increasing atomic number a point will therefore be reached where a 3_3 orbit will correspond to a firmer binding of the 19th electron than a 4_1 orbit.* . . . This cannot only be anticipated from a simple calculation but is confirmed in a striking way from an examination of the series spectra. While the spectrum of potassium indicates that the 4_1 orbit corresponds to a binding which is more than twice as firm as in a 3_3 orbit (corresponding to the first spectral term in the D series), the conditions are entirely different as soon as calcium is reached . . . Comparing the change in the relative firmness in the binding of the 19th electron (as inferred from a comparison of arc and spark spectra) in a 4_1 and 3_3 orbit for potassium and calcium we see that we must be prepared already for the next element, scandium, to find that the 3_3 orbit will correspond to a stronger binding of this electron than a 4_1 orbit . . . If we proceed to the following elements, a still larger number of 3_3 orbits will occur in the normal state of these atoms, since the number of such electron orbits will depend upon the firmness of their binding compared to the firmness with which an electron is bound in a 4_1 orbit, in which type of orbit at least the last captured electron in the atom may be assumed to move. We therefore meet conditions which are essentially different from those which we have considered in connection with the previous periods, so that here we have to do with *the successive development of one of the inner groups of electrons in the atom*, in this case with groups of electrons in 3-quantum orbits. Only when the development of this group has been completed may we expect to find once more a corresponding change in the properties of the elements with increasing atomic number such as we find in the preceding periods. The properties of the elements in the latter part of the fourth period show immediately that the group when completed will possess 18 electrons. Thus in krypton, for example, we may expect besides the groups of 1-, 2- and 3-quantum orbits a markedly symmetrical configuration of 8 electrons in 4-quantum orbits consisting of 4 electrons in 4_1 orbits and 4 electrons in 4_2 orbits."

For a closer consideration of the probable way in which the gradual

STRUCTURE OF THE ELEMENTS ON BOHR'S THEORY (1923).

Characteristic Quantum Numbers of Electron Groups →	1-Quantum Orbits.		2-Quantum Orbits.		3-Quantum Orbits.			4-Quantum Orbits.			5-Quantum Orbits.					6-Quantum Orbits.					7-Quantum Orbits.		
	1 ₁	2 ₁	2 ₂	3 ₁	3 ₂	3 ₃	4 ₁	4 ₂	4 ₃	4 ₄	5 ₁	5 ₂	5 ₃	5 ₄	5 ₅	6 ₁	6 ₂	6 ₃	6 ₄	6 ₅	6 ₆	7 ₁	7 ₂
H	1																						
He	2																						
Li	3	1																					
Be	4	2																					
B	5	2	(1)																				
Ne	10	4	4																				
Na	11	4	4			1																	
Mg	12	4	4			2																	
Al	13	4	4			2	1																
A	18	4	4		4	4	4																
K	19	4	4		4	4	4																
Ca	20	4	4		4	4	4																
Sc	21	4	4		4	4	4							1									
Ti	22	4	4		4	4	4							2	(2)								
Cu	29	4	4		6	6	6							1									
Zn	30	4	4		6	6	6							2									
Ga	31	4	4		6	6	6							2									
Kr	36	4	4		6	6	6							4									

Numbers of Electrons in the Various Groups.

Numbers of Electrons in the Various Groups.

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[illegible]

formation of the group of electrons having 3-quanta orbits takes place the reader is referred to Bohr's *The Theory of Spectra and Atomic Constitution*, wherein reasons are given for expecting 18 electrons in all in the 3-quanta group when this group is completed, the completion of this group (which is first realised in the case of copper, atomic number 29) corresponding to 6 electrons in the 3_1 orbit, 6 electrons in the 3_2 orbit, and 6 electrons in the 3_3 orbit. Further, Bohr gives reasons for expecting that such a completed 3-quanta group cannot occur as the *outermost* group in the case of a neutral atom, but only in positively charged ions, *i.e.* the cuprous ion Cu^+ . Evidence for this is afforded by the simple nature of the spectrum which is closely analogous to that of the sodium ion (where the outermost group is a completed 2-quanta group), the simplicity of a spectrum being associated with the degree of symmetry of the structure from which it originates. Bohr next proceeds to emphasise the importance (for atomic structure) of the phenomena of the magnetic properties and the colour exhibited by the atoms and ions of certain members of the fourth period. For this and further information the reader is again referred to Bohr's book. In general it may be said that the attempts to fix the structure of the elements of the remaining periods follows along lines similar to those already outlined.

In the foregoing table is given Bohr's summary of the probable structure of the atoms of the elements in so far as it is possible to assign a structure at the present time (1923). The table is taken from Bohr's article in *Nature*, Vol. **112**, 29, 1923.

Apart from X-ray and radioactive phenomena practically all the physical and chemical properties of the elements must be governed by the orbits of the last bound electrons in the atom. The relation between the degree of eccentricity of the orbits of the valency electrons and the electro-positive nature of the atom has already been mentioned. On the other hand, for elements of a pronounced electro-negative type the last bound electrons move in practically circular orbits which do not extend beyond previously bound groups, and they have therefore no tendency to part from the structure. Rather is there a tendency in these cases for the atom to pick up additional electrons and *thus approach one of the stable group structures characteristic of the inert gases*.

Finally reference may be made to what is called *the precession of an orbit*. The diagrammatic representation of Fig. 11 does not illustrate this behaviour. In the case of an atom containing a considerable number of electrons, say the potassium atom, the electron orbits which are characterised by great eccentricity (*i.e.* those in which the principal quantum number ($n + n'$) differs considerably from the other (n), as in a 4_1 or 5_1 orbit) will penetrate partly into the inner region already "occupied" by the earlier bound electrons. "Because of this circumstance the orbits will deviate very greatly from a simple Kepler motion, since they will consist of a *series* of successive outer loops that have the same form but each of which is turned through an appreciable angle relative to the preceding one." (The orbits in Fig. 11 show in effect

only *one* such loop for each case, *i.e.* each individual orbit of the type named is to be taken as repeating itself in space in a series of positions which differ successively from one another. This is termed precession.

The Structure of the Molecule and the Nature of the Chemical Bond in terms of Bohr's Theory.

So far we have dealt with the structure of individual atoms from the point of view of Bohr. The next problem would obviously be that of the molecule, of which the simplest type is the diatomic molecule, *e.g.* H_2 . Knowledge regarding the conditions of stability of such a structure is particularly important from the chemical standpoint, since all chemical reactions involve either the make or break of a bond between pairs of atoms. Unfortunately, however, Bohr has not as yet considered in any detail the question of the stability of even the simplest molecule. All that can be said at present is that undoubtedly quantum considerations, *i.e.* stationary states enter here, although it is not clear whether the treatment by means of two quantum numbers will be found to be adequate. The complexity of the problem arises from the fact that at least two nuclei operate on the mode of motion of the valency electrons, and, further, the motions of the nuclei themselves may be of importance.

Even in the case of molecular as distinct from atomic structures, however, emission spectra afford some information. Thus, whilst series spectra, such as the Balmer lines, originate in the separate atoms, *band spectra*, on the other hand, are due to molecules, *e.g.* the band spectrum of hydrogen. The fact that band spectra are so rich in lines is due to the complexity of the motion entailed by the vibrations of the atomic nuclei relative to each other and the rotations of the molecule as a whole. On the basis of general Bohr concepts it is concluded that the lines which constitute each band in a band spectrum are due to transitions between stationary states which differ as regards rotational motion. (Absorption band spectra of gases from the standpoint of stationary states are considered in a later section of this chapter.)

We have long been familiar with two types of chemical bond or union, namely that represented by the union of two carbon atoms in a saturated aliphatic molecule, and that represented by the union of sodium and chlorine in the sodium chloride molecule. In the latter it is practically certain that we are dealing with bound ions, an electron having passed from the sodium atom to the chlorine with the result that the force of attraction holding the molecule together is electrostatic. Such a link is known as polar, and the valency involved *electrovalency*. In the case of the typical organic molecule, however—and indeed in the case of the hydrogen molecule itself—there is no evidence of electronic transfer, the link is termed non-polar and is due to two electrons—one belonging to each atom—acting together in some manner. Such a bond is termed by Langmuir *covalent*. The importance of this type of link in chemical compounds, especially organic compounds, merits some further consideration. The following brief statement is virtually

a quotation from a paper by N. V. Sidgwick (*Trans. Faraday Soc.*, "Discussion on the Electronic Theory of Valency," 1923) in which Bohr's theory of atomic structure is taken as the basis

In connection with the covalent link, Sidgwick makes the assumption that the orbit of each shared electron includes both of the attached nuclei. This assumption has been found by Nicholson to be the only one which will account for the spectrum of molecular hydrogen; and it has also been put forward by N. P. Campbell (*Nature*, April, 1923) as an extension of Bohr's theory to non-polar linkages. Each orbit may be pictured as an ellipse with the nuclei at the foci, or more probably as a figure of 8 with a nucleus at the centre of each loop (Fig. 12).

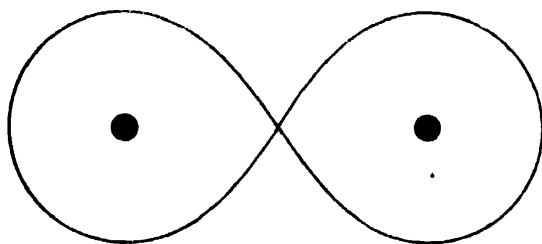


FIG. 12.

Each of the two covalent electrons has its own distinct binuclear orbit, possibly at right angles to one another, and, further, owing to mutual action each of the orbits undergoes slow rotation.

There are two obvious differences between such binuclear orbits and the simple

orbits of Bohr. The first is that the presence of a second nucleus in the orbit makes precession of the orbit impossible, unless indeed the same orbit successively includes several nuclei. The second is that all the electrons shared by any one atom have to pass through their perinuclea in due succession, and hence their periods must agree; moreover, in a chain of atoms the periods of all the binuclear orbits must be the same or must differ rationally.¹

It is an essential part of Bohr's theory that the valency electrons (with which we are concerned) pass very near the nucleus in the course of their motion, and that the powerful forces which come into play here are essential to the stability of the atom. Thus an orbit which surrounds and comes close to both of the two nuclei will form part of the constitution of both.

This theory explains why the groups attached, say to a carbon atom, retain their relative positions, in spite of the fact that each of the electrons holding them goes round the carbon nucleus; and these positions may be expected to have the tetrahedral symmetry which Bohr finds in the 4 orbits of an electron sub-group.

It also satisfies the condition of permitting the free rotation of singly linked carbon atoms. Singly linked carbon atoms are free to arrange themselves in the most stable configuration round the line joining them,

¹ As regards the concept of a binuclear orbit Sidgwick (*private communication*) points out that "the Bohr theory cannot at present decide either for or against this suggestion. The absence of precession makes it impossible to describe such orbits in terms of the n and k quantum numbers. Until more light has been thrown on the nature of the 'non-mechanical stress' which Bohr has recently found to exist between different orbits of the same atom, we do not know how much truth the hypothesis of binuclear orbits contains."

so that a compound of the formula $H_2XC - CH_2X$ can only occur in one form. As the single link is maintained for a great part of the time only by the attraction on the nuclei of a single electron, it is easy to see that such rotation must be possible.

It is further certain that with two doubly linked carbon atoms this freedom no longer exists; and that the compound $abC = Cab$ can exist in two forms, which only go over into one another under the ordinary conditions of chemical change. The relation between the groups attached to two such atoms is the same as if these atoms were part of a closed ring. In every way the double link appears as the limiting case of a ring reduced to its lowest terms. The tendency to rupture increases as the ring grows smaller, but the position of the attached groups remains the same as long as the ring or double link persists. The conception of binuclear orbits is in complete agreement with these facts. A carbon atom united to two others has two binuclear orbits connecting it to each, and these are normally inclined at the angle of $109^\circ 28'$. If these three atoms are joined up into a ring of less than 5 atoms, the orbits must be distorted from their normal positions, exactly as Baeyer assumed. This means that the two pairs of orbits, since their positions near each nucleus still tend to be inclined at the original angle, must become curved, and the more so the smaller the ring. Finally, in the doubly linked atoms, this curvature reaches a maximum, the orbits diverging as they leave one nucleus, and converging as they approach the other: this form being favoured by the mutual repulsion of the electrons, of which, as there are four altogether, at least two must at any time be in the region between the two nuclei. Two effects will thus be produced: first, the distortion of the orbits will diminish the stability of the linkage, and in proportion to the degree of distortion, which gives us a physical basis for the Baeyer strain theory with its later developments: and secondly, since the attachment of the two nuclei is maintained not by one electron pair but by two, and those somewhat remote, there will obviously be a restraint on the rotation of the atoms round the line joining them.

In fact this conception of the nature of the non-polar link gives us precisely what the chemical facts require—the idea of directed valencies, of a strain consequent on their deflection, and of the double link as the limiting case of a carbon ring.

Sidgwick has also extended the above mode of treatment to the case of co-ordinated compounds (*cf. Trans. Chem. Soc.*, **123**, 725 (1923).)

High Frequency Spectra of the Elements. Mosley's Relation.

By the high frequency spectrum is meant the X-ray spectrum which is obtained from a substance by bombarding the substance with β -rays. It has been pointed out in Vol. I., Chap. II., that the investigation of the structure of crystals by means of their X-ray spectra affords a means of determining with precision the wave-length of any homogeneous X-ray employed. X-rays only differ from light in possessing very much shorter

wave-lengths (of the order 10^{-8} cm.). The substance to be used as a source of X-rays forms the anticathode in a vacuum tube, and the beam of X-rays emitted as a result of bombardment by the cathode rays is characteristic of the substance forming the anticathode. In general the X-rays thus excited are not homogeneous. They consist of two or more wave-lengths which can be analysed and measured by means of the crystal acting as a grating. As a rule, however, one frequency is more prominent than the others, that is, the intensity of the resulting spectrum is greatest for one type, and for the sake of simplicity we shall consider these single frequencies as characteristic of the X-rays emanating from the substance examined. When the anticathode is of nickel, the characteristic wave-length of the X-ray produced is 1.10×10^{-8} cm. It follows, therefore, that a single quantum $h\nu$ of this type contains energy in amount 1.78×10^{-8} ergs. It is of interest to compare this quantity with the energy of the electron of the cathode stream which gave rise to the X-ray. Whiddington (*Proc. Camb. Phil. Soc.*, 1910) has shown that an electron of the cathode stream will not excite X-ray radiation unless its velocity exceeds a certain critical value, which varies with the nature of the material composing the anticathode. If the latter be of nickel the limiting velocity of the electron striking it is 6.17×10^{10} cm. per sec., or about one-fifth of the speed of light. Taking the mass of the electron to be 9.1×10^{-28} gram, the kinetic energy of the electron possessing the limiting speed is 1.7×10^{-8} erg, a quantity which is very nearly the same as the energy in a single quantum of the X-ray produced. Further, the investigation of the reverse process, *i.e.* the emission of an electron by means of X-rays, has shown that the kinetic energy of the electron is approximately equal to that of the cathode ray which excited the X-ray in the first instance. As Bragg remarks, "we are justified in assuming that these processes are actual examples of the give-and-take of radiant energy with which Planck's hypothesis is concerned."

Whiddington has also found that the limiting velocity of an electron just necessary to excite an X-ray from a particular element is proportional to the atomic weight of the element. Now we have seen that the frequency ν of the X-ray is proportional to the kinetic energy of the electron producing the ray. Hence the frequency of the X-ray is proportional to the square of the velocity of the electron and therefore to the square of the atomic weight. This serves as a useful guide in the choice of a substance for the anticathode which will produce an X-ray of a given kind.

In 1913 van den Broek (*Physikal. Zeitsch.*, **14**, 32) suggested, that in comparing elements with one another, the atomic number, that is, number which represents the position of the element in the periodic table is a far more fundamental quantity than the atomic weight itself. As a matter of fact the atomic number of an element is approximately one-half of the atomic weight, so that any quantity proportional to the atomic weight is likewise proportional to the atomic number.

The connection between the nature of an element and the frequency of the X-ray produced from it has been systematically studied by Moseley (*Phil. Mag.*, [vi.], **26**, 1024; *ibid.*, **27**, 703 (1914)). On plotting the square root of the maximum frequency of the X-ray produced from a given element against the atomic number of the element, for a whole series of elements, Moseley found that a simple linear relation connected the two quantities. This was true both for the K and L types of X-rays, types which differ from one another in intensity, the K type being produced from a "hard" bulb (high vacuum), the L type being produced from a "soft" bulb. Moseley's work extended by de Broglie (*Comptes Rendus*, **165**, 87, 352, 1917) proves that there exist but ninety-two elements, from the lightest, hydrogen, to the heaviest, uranium, and that these are built up one from the other by the successive addition of one and the same electrical element to the nucleus. In other words, the atomic number is not simply an ordinal but possesses an actual physical significance. The Rutherford atom-model, already discussed, suggests what this significance is.

The measurements of Rutherford and Geiger showed that the magnitude of the positive charge on the nucleus was Ne where e is identical with the magnitude of the charge on an electron, and N is a number approximately one-half the atomic weight. N is, in fact, a number identical with the atomic number. It is probable that the elements differ from one another in the magnitude of the nuclear charge, and it is reasonable to suppose that successive elements in a table of elements vary by the amount e on the nuclear charge. Regarding the nuclear charge of hydrogen atom as e itself, the succeeding elements will possess $2e$, $3e$, and so on, or in other words, the *atomic number indicates the magnitude of the nuclear charge*. If this be so, the various relations found between atomic number and other quantities serves to relate these quantities to the magnitude of the nuclear charge. The simplest form of Bohr's relation, already discussed, between the frequency of emitted radiation and the nuclear charge $E = Ne$ involves the square of the latter. In other words, the square root of the frequency emitted is proportional to E itself. Bohr's relation, in fact, is capable of predicting the characteristic X-ray radiation from an element of high atomic weight with considerable exactness.

Millikan (*Phys. Rev.* Aug., 1917) has pointed out several important conclusions which may be drawn from Moseley's law.

Thus, let us consider any two elements of atomic number N_1 and N_2 , with nuclear charges E_1 and E_2 , and suppose that ν_1 and ν_2 are the highest frequencies of the K or hard series of X-rays emitted by the elements in question. Then, according to Moseley's law—

$$\sqrt{\frac{\nu_1}{\nu_2}} = \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} = \frac{E_1^2}{E_2^2} = \frac{N_1^2}{N_2^2}$$

where λ_1 and λ_2 are the wave-lengths corresponding to the frequencies ν_1 and ν_2 . Let us now compare the elements tungsten and hydrogen. The wave-length λ_2 of the shortest X-ray emitted by tungsten is

0.185×10^{-8} cm. The atomic number of tungsten is 74. For hydrogen the atomic number is 1. Using the above relationship we find that the shortest X-ray which could be emitted by the hydrogen atom is $\lambda_1 = 101.3\mu\mu$. The head of the ultra-violet series of hydrogen lines recently discovered by Lyman is at $91.2\mu\mu$. In view of the fact that Moseley's relation, as stated above, is not absolutely exact, the agreement between these two results may be regarded as satisfactory. It is fairly certain, therefore, that the Lyman series of emission lines of hydrogen ending in the extreme ultra-violet is simply the K or hard series of the hydrogen X-ray spectrum. That is, in the case of hydrogen (owing to the small nuclear charge) the X-rays are situated in a region which may be termed ultra-violet. Further, it seems a just inference from similar considerations that the ordinary series of lines in the visible and near ultra-violet (*i.e.* the Balmer series of emission lines of hydrogen) with its head at $\lambda = 365\mu\mu$ is simply the L series of X-rays of this element. Likewise the series of lines in the infra-red region of the hydrogen spectrum, discovered by Paschen, may be identified with the M series of X-rays, for the M series represents X-rays even softer (*i.e.* of longer wave-length) than the L series. (Evidence for the existence of the M series has recently been obtained by electronic bombardment of a few of the elements of high atomic number.)

This similarity in behaviour of all elements as regards X-ray emission indicates similarity in structure in their innermost portions. An important conclusion regarding the innermost ring has been pointed out by Millikan, namely, that the radius of this ring is inversely proportional to the nuclear charge or atomic number. To show how this result is obtained it is necessary to revert to the Bohr theory of emission of radiation.

On the earlier theory of Bohr (namely that in which circular orbits were postulated), the frequency ν emitted is given by—

$$\nu = \frac{2\pi^2 mc^2 E^2}{h^3} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right).$$

To account for the shortest X-ray frequency of the K series it is necessary to set $\tau_2 = 1$ and $\tau_1 = \infty$. Whence—

$$\nu_K = \frac{2\pi^2 mc^2 E^2}{h^3}$$

Now the frequency of orbital motion ω has its maximum value when the electron is in the first orbit. For this case $\tau = 1$ and the expression already deduced (*cf.* equation (3) of this chapter) for ω becomes—

$$\omega = \frac{4\pi^2 mc^2 E^2}{h^3}$$

Whence $\nu_K/\omega = \frac{1}{2}$, *i.e.* the observed highest frequency of radiation emitted is proportional to the highest orbital frequency of the electron, the proportionality factor being the same for different elements.

Let us now consider an electron in an orbit of radius a . The force of attraction exerted on the electron by the nucleus is Ec/a^2 . If the electron has a mass m and an orbital frequency ω the equilibrium condition is given by—

$$\frac{Ec}{a^2} = (2\pi\omega)^2 m \cdot a.$$

Hence for any two different elements we have—

$$\frac{\omega_1^2}{\omega_2^2} = \frac{E_1 a_2^3}{E_2 a_1^3} = \frac{N_1 a_2^3}{N_2 a_1^3}$$

where N_1 and N_2 are the atomic numbers of the elements. If we now regard a_1 and a_2 as referring to the innermost orbit of each element and consequently ascribe maximum values to ω_1 and ω_2 , it follows, from the relation just obtained, that—

$$\frac{\omega_1}{\omega_2} = \frac{\nu_1}{\nu_2}$$

where ν_1 and ν_2 are the highest frequencies which the elements can emit. From Moseley's law we have—

$$\frac{\nu_1}{\nu_2} = \frac{E_1^2}{E_2^2} = \frac{N_1^2}{N_2^2}$$

Hence

$$\frac{N_1 a_2^3}{N_2 a_1^3} = \frac{\omega_1^2}{\omega_2^2} = \frac{\nu_1^2}{\nu_2^2} = \frac{N_1^4}{N_2^4}$$

or

$$\frac{a_2}{a_1} = \frac{N_1}{N_2},$$

i.e. the radius of the innermost ring is inversely proportional to the nuclear charge or atomic number.

Further, Moseley has found that the L series of X-rays progress by steps just as do the K series for different elements, the frequencies of the L series being about one-eighth as great as those of the K series. This shows that if there is an innermost electronic orbit there must likewise be a second orbit in all elements, the radius of which is given by a relation of the form, $\omega_1^2/\omega_2^2 = N_1 a_2^3/N_2 a_1^3$, to be about $8^{2/3}$ or four times as great as that of the first orbit.

Again it has been found experimentally that the following relation is true—

$$\nu_{K\beta} = \nu_{Ka} = \nu_{La}.$$

According to Bohr the longest wave-length line of the K series, that is the α line, is due to the electron passing from orbit 2 to orbit 1, the change in energy being $W_2 - W_1$. The next longest wave-length line, the β line, is due to the passage from orbit 3 to orbit 1 with a change in energy $W_3 - W_1$, and so on. The longest wave-length line of the L series, namely the α line of that series, is due to passage of the electron from orbit 3 to orbit 2 with a change in energy of $W_3 - W_2$; the β -

line of this series being produced by passage from orbit 4 to orbit 2 and so on. Hence if the frequency is in all cases due solely to the change in energy it follows that—

$$\frac{W_1}{W_2} - \frac{W_1}{W_1} = \frac{v_k}{v_l} \beta$$

whence

$$\frac{W_3}{W_2} - \frac{W_2}{W_2} = \frac{v_k}{v_l} \beta$$

But

$$\frac{W_3}{W_2} - \frac{W_2}{W_2} = \frac{v_l}{v_1} \alpha$$

Therefore

$$v_l \beta = v_k \alpha = v_1 \alpha$$

The fact that this relationship holds is strong evidence in favour of Bohr's views regarding the source and magnitude of the frequency of radiation emitted in general.

Characteristic Infra-red Frequency and Atomic Number.

An interesting relationship has been pointed out by Allen (*Proc. Roy. Soc., A*, **94**, 100 (1917)) between the atomic number and the infra-red frequency which accounts approximately for the atomic heat of the element. Writing N for the atomic number and ν for the frequency of a given element, Allen's relationship is—

$$N\nu = n\nu_A$$

where n is an integer called the frequency number, and ν_A is a fundamental constant the same for all elements. The mean value for ν_A is 21.3×10^{12} . The following table illustrates the above relation. The experimental values of ν for the various elements (obtained from atomic heat measurements of Nernst, Griffiths, and Keesom-Onnes) have been multiplied by the atomic number N .—

Element	N	$N \times 10^{-12}$		
		Nernst	Griffiths	
Al	13	5×21.6	5×21.4	5×21.5
Fe	26	—	10×20.9	10×20.9
Cu	29	9×21.3	9×21.9	9×21.3
Zn	30	7×20.6	7×20.6	7×20.6
Ag	47	10×21.2	10×21.1	10×21.1
Cd	48	—	8×21.1	8×21.1
Hg	80	8×20.2	—	8×20.2
Pb	82	7×22.2	7×22.5	21.6

The above relationship is empirical and its full significance has not yet been determined. It may be pointed out, however, that Biltz has shown the characteristic infra-red frequency ν of the elements to be a periodic function of the atomic weight, and therefore of the atomic number. Since ν_A is a constant it follows that n must likewise vary in a periodic manner with the atomic weight or number. This is not the same thing, however, as explaining the significance of n .

Infra-red Absorption Spectra of Gases.

In Chapter IV. an account has been given of the infra-red absorption bands exhibited by gases, these bands being attributed by Bjerrum to molecular rotations. Into Bjerrum's treatment considerations which are characteristic of Bohr's concepts do not enter. In view of the success which has attended Bohr's treatment of electronic motion in atomic structures it is instructive to see to what results similar considerations lead when applied to the rotations of molecules.

The fundamental idea which emerges from Bohr's work is that the concept of quantisation is not to be applied to energy—as was done in the earlier stages of the quantum theory—but essentially to *angular momentum*. (Note that we are here only making use of Bohr's earlier concept; quantisation of eccentricity is not considered.) This is expressed by writing —

Angular momentum of a particle in the m th orbit = $mh/2\pi$.

Considering the case of rotation of a molecule with a fixed moment of inertia, I , the angular momentum is given by $I\omega$, where ω is the angular velocity. The angular velocity ω is $2\pi\bar{\nu}$ where $\bar{\nu}$ is the frequency of rotation. Since we have assumed the moment of inertia to be constant it follows that the different stationary states are not represented by orbits of different radius but simply by different speeds of rotation in one and the same orbit. Applying the idea that angular momentum is capable of quantisation, that is, takes on discrete values, we can say that the angular momentum of rotation can be written as 1, 2, 3 or in general m times a constant, this constant being $h/2\pi$. Hence for the general case we write—

$$I \cdot 2\pi\bar{\nu} = mh/2\pi$$

or

$$\bar{\nu} = mh/4\pi^2 I$$

It is evident that $\bar{\nu}$ can take on a series of values according to the value ascribed to m . It is essential, however, to observe that in accordance with Bohr's theory—and here we depart entirely from Bjerrum's original treatment—the term $\bar{\nu}$ does not give the frequency of a rotational band observable by spectroscopic means, for $\bar{\nu}$ is the frequency of rotation in a given stationary state, *i.e.* a non-radiating, non-absorbing state. Whilst therefore the above expression for $\bar{\nu}$ may be true, it is not the one which must be sought in order to account for bands, if Bohr's concept be applicable. The necessary mode of procedure is given below. The above considerations have been introduced with the purpose of indicating the distinction which must be drawn between the frequency of rotation in a steady state and the frequency of radiation emitted or absorbed as a result of the system changing from one stationary state to another. It is the latter condition which has now to be considered.

The energy of rotation of a molecule is given in general by $\frac{1}{2} I \omega^2$, where ω is the angular velocity. We have already assumed that for the m th stationary state

$$I\omega = mh/2\pi.$$

Hence the energy of rotation may be written as—

$$W_m = m^2 h^2 / 8\pi^2 I.$$

Following Bohr's concept of the derivation of the frequencies absorbed or radiated by the molecule as due to the absorption or emission of quanta in the discontinuous change from one stationary state to another, it will be seen that for the change from the $(m - 1)$ th rotational state to the m th rotational state of the molecule, the energy absorbed is given by—

$$\begin{aligned} h\nu_{(m-1), m} &= W_m - W_{m-1} \\ \text{or } h\nu_{m-1, m} &= \frac{h^2}{8\pi^2 I} (m^2 - (m-1)^2) \\ &= \frac{2m-1}{2} \cdot \frac{h^2}{4\pi^2 I}. \end{aligned}$$

Similarly, for the change from the m th to the $m + 1$ th state,

$$h\nu_{m, m+1} = \frac{2m+1}{2} \cdot \frac{h^2}{4\pi^2 I}.$$

Hence the difference in the consecutive frequencies $\nu_{m, m+1}$ and $\nu_{m-1, m}$ (these frequencies being observable spectroscopically) is given by $h/4\pi^2 I$, a quantity *independent of the value of m* . It is evident therefore that the rotational absorption spectrum of a gas should consist of a series of frequencies¹ in arithmetic progression, their values being given by—

$$\frac{h}{8\pi^2 I}, \frac{3h}{8\pi^2 I}, \frac{5h}{8\pi^2 I}, \dots, \frac{(2m-1)h}{8\pi^2 I}.$$

The rotational spectrum predicted on the above basis differs from that originally suggested by Bjerrum, whose method leads to the series—

$$\frac{h}{4\pi^2 I}, \frac{2h}{4\pi^2 I}, \frac{3h}{4\pi^2 I}, \text{ etc.,}$$

on the basis that absorption or emission of a particular frequency is due to the molecule *in* one particular state and not a change from one state to another.

It will be observed that both series give the same value to the difference between any two consecutive frequencies. Actually the data available in connection with the far infra-red bands which have been observed directly by Rubens and indirectly by Sletor (*cf.* Chapter IV.) for the case of water vapour barely permit of choosing between the two series. The following table contains the bands to be expected on the Bohr method of treating rotations along with those given by Bjerrum. On the whole, Bjerrum's values show better agreement with the experimental observations.

As pointed out in Chapter IV., Bjerrum found that a constant fre-

¹ In Appendix VI. reasons are given which would lead us to expect that in general the first member of the series would be $3h/8\pi^2 I$ rather than $h/8\pi^2 I$.

quency difference of 1.73×10^{12} characterised the water bands. This frequency difference (which is equivalent to a wave-length of 173.4μ) is given by $h/4\pi^2I$. On the Bohr basis the first * band (*i.e.* longest wave-length) is given by $h/8\pi^2I$, that is the longest wave-length is 173.4×2 or 346.8μ . The second band characterised by $3h/8\pi^2I$ is therefore in wave-lengths $346.8/3$ or 115.6μ . The third band characterised by $5h/8\pi^2I$ is therefore $346.8/5$ or 69.4μ , the fourth band being $346.8/7$ or 49.0μ , and so on. Each of these bands corresponds to setting m equal to 1, 2, 3, 4, etc., in the series formula given above.

INFRA-RED BANDS OF WATER VAPOUR.

Wave-length, in μ .	L. von Bahr. (Inferred from analysis of short Infra-red Band.)	Sleator.	Wave-length Calculated on Bohr Basis	Wave-length Calculated on Bjerrum Series.
10.9			10.5 ⁽¹⁷⁾	10.8 ⁽¹⁶⁾
11.6			11.2 ⁽¹⁶⁾	11.6 ⁽¹⁵⁾
12.4			12.0 ⁽¹⁵⁾	12.4 ⁽¹⁴⁾
13.4			12.8 ⁽¹⁴⁾	13.3 ⁽¹³⁾
14.3			13.9 ⁽¹³⁾	14.4 ⁽¹²⁾
15.7			15.1 ⁽¹²⁾	15.8 ⁽¹¹⁾
17.5			16.5 ⁽¹¹⁾	17.3 ⁽¹⁰⁾
19.2	19.3	—	18.3 ⁽¹⁰⁾	19.3 ⁽⁹⁾
19.7	19.9	—		
20.5	20.6	—	20.4 ⁽⁹⁾	
21.6	21.8	—		
22.9	23.3	—	23.1 ⁽⁸⁾	
23.8	24.3			
25.0	25.2	25.3	—	24.7 ⁽⁷⁾
26.6	26.9	26.9	26.7 ⁽⁷⁾	
28.9	28.3	28.9	—	28.9 ⁽⁶⁾
30.6	30.6	30.6	31.5 ⁽⁶⁾	
32.9	32.9	34.2	—	
35.7	35.7	36.7	—	34.7 ⁽⁵⁾
40.0	38.8	40.3	38.5 ⁽⁵⁾	
—	42	43		43.3 ⁽⁴⁾
44.1	45			
—	47.5			
49.0	49.5	51.0	49.0 ⁽⁴⁾	
57.7	55	56.8	—	57.8 ⁽³⁾
65.8	62.5	65.3		
72.2	69.5	72.5	69.4 ⁽³⁾	
78.0	80	81.6		
(83)				
(92)	91	92.5	—	86.6 ⁽²⁾
—	—	101		
105.8	109			
—	—	113	115.6 ⁽²⁾	
132.2	126	135		
175.6	171	—	—	173.4 ⁽¹⁾
265.7	240-250			
—	385-398	—	346.8 ⁽¹⁾	

* Cf. preceding footnote.

The numbers in brackets in the fourth column denote the values of m , the corresponding numbers in the final column denoting the values of n , n being the symbol employed in Bjerrum's rotational expression in Chapter IV. It is evident from a comparison of the results obtained by the two distinct methods of treating infra-red absorption spectra that much remains to be done before a satisfactory mechanism of the phenomenon is forthcoming.

As pointed out in Chapter IV., in Bjerrum's original treatment of the complex nature of the *short* infra-red band there is no satisfactory reason given for the absence of the central frequency due to vibration itself as well as for the absence of a contiguous sub-band on the shorter wave side of the centre. The absence of the central frequency may be anticipated on the basis of a certain assumption if the behaviour of the molecule be regarded from the point of view of Bohr's theory of stationary states, as applied to the vibrations of the atoms as well as to the rotations of the molecule.

Let us denote by n the n th stationary state of atomic *vibration*, by m the m th stationary state of *rotation* of the molecule. The molecule has then rotational energy, $W_m = \frac{h^2}{8\pi^2 I} \cdot m^2$, and vibrational energy $n h \nu_p$ where ν_p denotes vibration frequency.

For the change from the state represented by (n, m) to the state (n', m') let us assume that one quantum of energy denoted by $h\nu_{m, m'}^{n, n'}$ is absorbed. This quantity represents the increase in energy in passing from the first state to the second. In other words, $h\nu_{m, m'}^{n, n'}$ can be equated to the difference in the energy contents of the two states. That is,

$$h\nu_{m, m'}^{n, n'} = h\nu_p(n' - n) + \frac{h^2}{8\pi^2 I}(m'^2 - m^2)$$

$$\nu_{m, m'}^{n, n'} = \nu_p(n' - n) + \frac{h}{8\pi^2 I}(m'^2 - m^2)$$

Similarly for the change from the state represented by, say, (n, m) to the state $(n', m - 1)$, if one quantum of energy $h\nu_{m, m-1}^{n, n'}$ be absorbed, it follows that,

$$\nu_{m, m-1}^{n, n'} = \nu_p(n' - n) - \frac{h}{8\pi^2 I}(m^2 - (m - 1)^2)$$

$$\text{or} \quad \nu_{m, m-1}^{n, n'} = \nu_p(n' - n) - \frac{2m - 1}{2} \cdot \frac{h}{4\pi^2 I} \quad \quad \quad (a)$$

Also, for the change from the state $(n', m - 1)$ to the state (n'', m) we have,

$$\nu_{m-1, m}^{n', n''} = \nu_p(n'' - n') + \frac{2m - 1}{2} \cdot \frac{h}{4\pi^2 I} \quad \quad \quad (b)$$

In equations (a) and (b) the symbols are employed in the sense that n'' represents a state of greater vibrational energy than n' , *i.e.*

energy is absorbed in passing from n' to n'' . Similarly the m th rotational state contains more energy than the $(m - 1)$ th state. It will be observed that whilst radiation is being absorbed by the change in vibrational state from n' to n'' , the rotational energy state may either increase or diminish. Hence when vibration and rotation are compounded we should find sub-bands on both sides of a central position. In other words, the above expressions for ν represent a series of pairs of absorption sub-bands on either side of the hypothetical central frequency $\nu_r(n'' - n')$, the distance between two consecutive sub-bands on either side being $\Delta\nu = h/4\pi^2 I = \text{constant}$. The hypothetical central frequency $\nu_r(n'' - n')$ is due to atomic vibration unaccompanied by molecular rotation, and since this band is not observed experimentally we may conclude that a change in the frequency of vibration (*i.e.* a change from one vibrational state to another which on Bohr's basis is necessary to originate a vibrational band) is not possible without a *simultaneous* change in the rotation of the molecule as a whole. This is very different from saying that there are no rotationless molecules in the system. There probably are such present. All that the above conclusion requires (to explain the absence of the central frequency in the short infra-red) is that rotationless molecules are completely analogous to molecules which are rotating *in* a certain state. So long as a given rotational state is *maintained* it is apparently impossible for a change in a vibrational state to take place. If movement from one vibrational state to another is prevented there will be no evidence, of a spectroscopic kind, for vibrational energy. The above treatment is due essentially to Kratzer (*Zeitsch. Physik*, **3**, 289, 1920) whose work followed closely on that of Heurlinger (*ibid.*, **1**, 82, 1920). Kratzer's theory is further considered in Appendix VI.

Einstein's Use of a Generalised Bohr Model to deduce the Radiation Law of Planck.

(*cf.* Einstein, *Ber. Deutsch. phys. Ges.*, **18**, 318, 1916, *Physikal. Zeitsch.*, **18**, 121, 1917.)

The most unsatisfactory part of Planck's treatment of the quantum theory (and this applies to both the first and second formulation) is the introduction of classical electrodynamic relations into a process of analysis the essential feature of which is the discarding of the fundamental basis from which these same relations are deduced.

In his first formulation Planck combines the concept of discontinuous absorption and emission on the part of an oscillator with the essentially classical relation:—

$$U_\nu = \frac{8\pi\nu^2}{c^3} E_{\text{average}}$$

In his second formulation it is true that classical absorption of radiation is retained, but it is necessary, in order to arrive at the correct radiation formula, to assume a very arbitrary dependence of the probability of discontinuous emission by an oscillator on the density of radiant

energy surrounding it. It is difficult, however, to see how continuous absorption of energy by an oscillator according to the classical laws can take place without accompanying emission of radiation in the same sense. An harmonic oscillator is alternately retarded and accelerated in its path, and on classical views should both absorb and radiate continuously. Thus, it is obvious that the arguments used in either form of the quantum theory are not free from self-contradiction.

For this reason Einstein (*loc. cit.*) has attempted to obtain Planck's relation for black body radiation without the necessity of specifying in any detailed manner the mechanism of the interaction between oscillators and radiation, *i.e.* without introducing classical laws into what must be essentially a quantum phenomenon. The method is as follows.

The marked success of Bohr's theory of spectra makes it appear likely that the fundamental basis of the quantum theory must be contained therein. Einstein therefore makes use of a generalised Bohr model in place of the linear oscillator used by Planck, as the material particle or molecule which is in equilibrium with black body radiation. The essential quantum feature of a Bohr model is its ability to assume *only* a discrete series of stable states with definite energy contents. This is all we require to know of the structure of the molecule or oscillator in order to arrive at a radiation expression having the same general form as that of Planck.

Consider a gas composed of similar molecules and in equilibrium with temperature radiation. Each molecule is only capable of existing in a discrete series of states Z_1, Z_2, Z_3 , etc., with energy contents E_1, E_2, E_3 , etc. It follows in the well-known manner from statistical treatment that the probability W_n of the state Z_n , or the relative number of molecules in the state Z_n , is given by:—

$$W_n = A f_n e^{-E_n/kT}$$

where the constant A , although it may not be independent of temperature, is independent of the state n . f_n is a weight (*gewicht*) factor characteristic of the state of energy E_n and denotes the intrinsic probability of the state in question. In many cases all states of a molecule may be regarded as having the same intrinsic probability, namely unity, but this is not necessarily true for quantum systems in which the same energy content E_n may be made up in different ways (*cf.* Sommerfeld's generalised Bohr orbits). In the present case we shall take f_n as unity.

We shall now assume that a molecule can pass from the state Z_n to the state Z_m by absorption of radiation (*i.e.* $Z_m > Z_n$), the radiation having a definite frequency ν which may be more explicitly denoted by $\nu_{n,m}$. Similarly the oscillator can pass from Z_m to Z_n by emission of similar radiation. The corresponding energy converted is $E_m - E_n$. This will in general be possible for each combination of the two indices n and m . Statistical equilibrium will persist for each of these elementary processes in order that temperature equilibrium may persist. We shall limit ourselves to the elementary process belonging to the definite pair of indices (n, m) .

In the first place, a change of state from Z_m to Z_n will occur with *emission* of energy $E_m - E_n$. Einstein considers that such an emission of energy by a molecule in the Z_m state will be spontaneous in character, and will follow the same statistical law as that which governs the disintegration of the radioactive bodies, i.e. the number of transitions from the state Z_m to the state Z_n due to this effect may be written as equal to :—

$$A_m^m N_m$$

where N_m is the number of molecules in the state Z_m , and A_m^m is a constant specific to the combination of the states Z_m and Z_n , and independent of any external effects.

A different law must regulate the processes called into existence by the effect of the external radiation. The process of *absorption* is brought about by the radiation field in which the molecule lies, and is taken as proportional to the radiation density of that frequency which corresponds to the subsequent transition. The number of transitions per unit time of Z_n molecules into Z_m molecules is given by :—

$$B_n^m N_n u_\nu$$

where N_n is the equilibrium number of Z_n molecules, and B_n^m is a constant characteristic of the combination (n, m) . However, under the influence of radiation, two things may happen to a molecule. A Z_n molecule may pass from the state Z_n to Z_m by taking up energy; this is "positive absorption," just considered. Or, it may happen, as a result of the phase relation between the radiation field and the molecule, that the molecule *loses energy through the action of the radiation*, and by such "negative absorption" a Z_m molecule may pass to the state Z_n . The rate of this process will also be proportional to u_ν , so that the number of Z_m molecules which pass to the state Z_n per unit time as a consequence of this negative absorption is :—

$$B_m^n N_m u_\nu$$

where B_m^n is *another* constant specific to the combination (m, n) .

As the condition for statistical equilibrium we have :—

$$A_m^m N_m + B_m^n N_m u_\nu = B_n^m N_n u_\nu$$

On the other hand we have :—

$$\frac{N_m}{N_n} = \frac{\rho_m e^{-E_m/kT}}{\rho_n e^{-E_n/kT}} = \frac{\rho_m}{\rho_n} e^{-(E_m - E_n)/kT}$$

Combining these two equations we obtain :—

$$A_m^m \rho_m = u_\nu \{ B_n^m \rho_n e^{(E_m - E_n)/kT} - B_m^n \rho_m \}$$

In this equation u_ν is the radiation density for that frequency ν which is absorbed or emitted in the changes $Z_n \rightarrow Z_m$ or $Z_m \rightarrow Z_n$ respectively.

Since u_ν increases without limit as T increases, it is necessary (in order to keep the whole right hand expression finite) that the quantity within the bracket should become zero at very high values of T . Since under these conditions the exponential term becomes unity it follows that—

$$B_m^n \rho_n = B_n^n \rho_m.$$

Further, for brevity let us write $A_m^n B_m^n = a_{m,n}$. It follows then that—

$$u_\nu = \frac{a_{m,n} \nu}{e^{(E_m - E_n)/kT} - 1}.$$

This is the relation between radiation density and temperature given by the Planck equation. The constants $a_{m,n}$ and $(E_m - E_n)$ could be directly determined if we were in possession of a modified electrodynamics in the sense of the quantum theory. However, $a_{m,n}$ and $(E_m - E_n)$ cannot depend on the particular nature of the molecule, but only on the frequency ν , since u_ν is a *universal* function of ν and T .

By comparison with Wien's displacement law, $u_\nu = \nu^3 f(\frac{\nu}{T})$, it follows that $a_{m,n}$ and $(E_m - E_n)$ must be proportional to the third and the first powers of ν respectively. Accordingly we can write —

$$E_m - E_n = h\nu$$

where a and h are constants. It is noteworthy that the latter result is identical with the second fundamental hypothesis of Bohr's theory of spectra.

Parson's Magnetron and the Structure of the Atom

Hitherto, in dealing with the problem of atomic structure, we have regarded the electron as a minute discrete particle of electricity or matter, assumed to be spherical, and capable of movement "inside" the atom in certain orbits, the velocity of movement being relatively small compared with the velocity of light. A new concept has been introduced, however, in connection with the electron which must be very briefly discussed. According to this view the electron itself is a tiny ring or annulus carrying a negative charge. The ring is regarded as rotating continuously with a peripheral velocity which is of the same order as that of light. This is equivalent to a circuit current, analogous to the Ampère currents assumed to account for magnetism, and consequently such a structure possesses magnetic properties. For this reason, A. L. Parson, to whom this concept of the electron is due (*Smithsonian Inst. Pub.*, **65**, No. 11, 1915), substitutes the word *magnetron* in place of electron.

The term magnetron was first introduced by Weiss in 1911 (*cf.* N. Campbell's *Modern Electrical Theory*). On the basis of the electron

theory of paramagnetism an expression has been deduced for the *susceptibility* according to which this quantity should be proportional to M^2/T , where M is the magnetic moment of a molecule and T is the absolute temperature. Weiss observed that in the case of magnetite over a certain temperature range the curve connecting the susceptibility with the reciprocal of the temperature was not a straight line through the origin, as it should have been, but consisted of a series of lines separated by definite differences in the value of the susceptibility. This was ascribed by Weiss to abrupt, discontinuous variations in the value of the molecular magnetic moment M , and Weiss further showed that the various observed values were all even multiples of a certain quantity to which he gave the name the magneton. The magnitude (*i.e.* the moment) of the magneton is the same as that which would be produced by a rotating electron revolving in an orbit of radius 10^{-8} cm. with a frequency of 10^{11} per second approximately. Weiss of course kept to the classical concept of the electron.

In the case of Parson's ring electron or circuit current the radius of the ring is estimated to be about 1.5×10^{-8} cm., that is a quantity somewhat less than the accepted value for the diameter of an atom. Parson's theory of atomic structure based upon the magneton hypothesis may be summarised as follows:—

The positive charge in the neutral atom, which must be present to balance the negative charges of the magnetons is regarded as a sphere of uniform positive electrification possessing a volume which is proportional to the number of magnetons which it contains. That is, the distribution of the positive charge is once more treated as in the original theory of atomic structure first advanced by Sir J. J. Thomson (*cf.* Chap. I, Vol. I). This positive sphere is regarded as having the properties of an elastic solid and "is surrounded by an atmosphere or envelope of very low charge density which is also elastic". Given this distribution, Parson shows that a group of eight magnetons may be arranged symmetrically round the sphere so as to give a stable configuration, and even with atoms possessing a larger number of magnetons, a similar distribution of eight is assumed. Such an arrangement obviously recalls the Abegg-Bodlander theory of valency, according to which the natural number of valencies is eight, though all these are not effective as far as another atom is concerned. To explain the existence of the long periods in the period classification as well as the properties of certain elements contained therein, it is necessary to assume a certain "hindrance" to the formation of the normal number of eight magnetons.

On the basis of these assumptions Parson discusses the single magnetic attraction between two such magnetons, the tendency to form the group of eight, the residual valency effect and the electrical polarisation set up by a magneton of the above type. On the basis of this atomic structure Parson has made a rough calculation of the heat of dissociation of hydrogen, obtaining the value 135,000 cal. per gram-molecule; Langmuir's value being of the order 85,000 cal.

One of the most obvious advantages of the Parson magneton is that

it affords a rational basis for the assumption made by Bohr, *viz.* that an electron rotating in a stable orbit does not radiate. A rotating electron—as hitherto envisaged—suffers an effective inward acceleration in rotating, and hence, on the basis of the classical electromagnetic theory, it should emit radiation continuously, its orbit becoming smaller until it falls into the centre of the atom. On the basis of the classical electromagnetic theory it is also known that the greater the number of electrons rotating in a ring the less the radiation from the ring. The Parson ring magneton is equivalent to a continuous series of charges, and consequently such a ring, howsoever great its velocity, will not radiate at all. This carries out Bohr's idea of the absence of radiation from an electron *in* an orbit.

On the other hand, one of the most obvious disadvantages of Parson's theory of atomic structure lies in the assumption of a uniform positive sphere of electricity, for on such a basis it is quite impossible to account for the large angle scattering of α rays observed by Rutherford. The point is therefore whether we can retain the advantage of the ring electron or magneton and at the same time get rid of the hypothesis of the positive sphere, by substituting for it the nucleus idea of Rutherford. The difficulty, as already pointed out, consists in the fact that an atom consisting of a nucleus surrounded by an atmosphere of magnetons would be an unstable system. The problem has been discussed in a preliminary manner by D. L. Webster (*J. Amer. Chem. Soc.*, **40**, 375, 1918).

From what has been said it will be obvious that the magneton theory of atomic structure as developed by Parson is still in a rudimentary stage. A critical review of this theory will be found in the (*Proc. Phys. Soc. (Lond.)*, **31**, 49, 1919).

The Lewis-Langmuir Atomic Model.

Within recent years an atomic model has been suggested by G. N. Lewis and later expanded in general scope and significance by I. Langmuir. It has attracted considerable attention owing to the remarkable manner in which it summarises the essentially chemical properties of atoms and molecules, *e.g.* the periodicity of properties as a function of atomic weight or number, the model being in fact designed for this purpose. The Lewis-Langmuir model is essentially a static one—in contradistinction to the model of Bohr—the electrons, when the atom is in a stable configuration, being fixed in certain positions¹ with respect to the nucleus. The concept of orbital motion is wholly wanting in this model. On the other hand, to account for emission and absorption spectra it is necessary to postulate that an electron can take up positions of equilibrium corresponding to different radial distances from the nucleus. The development of this atomic model has involved essentially geometrical considerations. For this reason a detailed consideration of the nature and applicability of this atomic model does not

¹ Or vibrating with very small amplitude through such positions.

properly fall within the scope of the present volume. Attention must be drawn, however, to a preliminary attempt which has been made by Langmuir (*Science*, **53**, 290 (1921)) to deal with an essentially static atom (*i.e.* one in which revolution of the electrons around the nucleus is excluded), from the point of view of quantum considerations, for it is obvious that however successful an atomic model may be in predicting chemical properties it cannot be regarded as a satisfactory solution of the problem of atomic structure and stability until it can be shown to possess a mechanical basis. Langmuir's treatment is as follows:—

It is assumed, in the first place, that Coulomb's law holds for the attraction between the nucleus and an electron. To account for the fact that the electrons do not fall into the nucleus it is necessary to assume some repulsive force. On Bohr's theory the requisite repulsive force is the centrifugal force due to rotation of the electrons about the nucleus. In the case of a static atom this is not possible. It is necessary to postulate some law of repulsive force between an electron and the positive nucleus which will produce an effect equivalent to the centrifugal force of Bohr's theory.

On Bohr's theory, as already pointed out, the average kinetic energy of the electrons in an atom is one half as great as the average potential energy, but opposite in sign. Langmuir assumes that "this energy, which Bohr called kinetic, is another form of potential energy, dependent upon certain quantum changes *in* the electron. From this potential energy it is then easy to determine the law of repulsive force."

As a result of his analysis Langmuir concludes that the force between a nucleus of charge Ze and an electron of charge e is made up of two parts which act independently. The first is the attraction given by—

$$F_c = \frac{Ze^2}{r^2} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where r is the distance between nucleus and electron.

The second force, called the *quantum force* is a repulsion F_q given by—

$$F_q = \frac{1}{mr^3} \left(\frac{nh\sqrt{2}}{2\pi} \right)^2 \quad (2)$$

where m is the mass of the electron and n is an integer denoting the *quantum state* of the electron.

To give a physical meaning to the quantum state of an electron it is necessary to regard n as differing fundamentally from the symbols employed in Bohr's treatment. Langmuir (*Brit. Assoc. Report*, 1921, p. 478) makes the distinction in the following words. "Bohr speaks of a unquantic or diquantic orbit of an electron, but seems to consider that the electron itself does not change in passing from one orbit to another. Is it not more logical to think of the orbit as resulting from the properties of the electron and to consider that quantum changes occurring in radiation cause discontinuous changes in the structure of the electron?" . . . "If we are to have a mechanism at all it appears

logical to look for it within the electron itself, even if this does lead us at first to unpleasant complications in our conception of the electron." In other words, the electron itself, on Langmuir's view, has to be quantised.¹

It will be observed that equation (2) is very similar to the law of repulsion between monatomic—or "thermally monatomic"—gas molecules as deduced by Nernst when the gas is in the degraded state (*cf.* Chap. IV.), Nernst's expression being—

$$k_0 = \frac{1}{mr^4} \frac{h^2}{4\pi}$$

where, however, m is the mass of the molecule

It is noteworthy that the repulsive force as given by equation (2) is independent of the nuclear and electronic charges. "It is to be noted especially that an electron which has not undergone any quantum change, and for which therefore $n = 0$, follows Coulomb's law accurately. Thus presumably β rays in passing through an atom will be acted on only by the usual law." A free electron, *i.e.* free with respect to the nucleus, is one for which $n = 0$.

By equating the forces of attraction and repulsion it follows that an electron will be in an equilibrium position when it is at a distance a from the nucleus defined by—

$$a = \frac{n^2 a_0}{Z} \quad (3)$$

where a_0 is given by—

$$a_0 = \frac{h^2}{4\pi^2 m e^2} \quad (4)$$

This result (equations (3) and (4)) is identical with that for the radius of the orbit on Bohr's theory, but, of course, the law of force was chosen to give this result. It will be observed that a varies with the value of n , *i.e.* there are a number of equilibrium positions possible to the electron.

If W be the total energy of the atom with sign reversed, then W is the work required to remove the electron to an infinite distance, so that we can write—

$$\begin{aligned} W &= - \int_r^\infty \frac{Ze^2}{r^2} dr + \int_0^r \frac{1}{m} \left(\frac{nh}{2\pi} \right)^2 \frac{dr}{r^3} \\ &= \frac{Ze^2}{r} - \frac{1}{2m} \left(\frac{nh}{2\pi} \right)^2 \frac{1}{r^2} \\ \frac{W}{W_0} &= \frac{2Za_0}{r} - \frac{n^2 a_0^2}{r^2} \end{aligned} \quad (5)$$

where

$$W_0 = 2\pi^2 m e^4 / h^2 \quad (6)$$

¹ An alternative treatment, leading to Langmuir's equation (2), which does not, however, involve such revolutionary ideas as regards structure of the electron, is discussed later in connection with the Whittaker-Lewing model.

(W_0 represents the energy required to dissociate completely an atomic system consisting initially of a nucleus carrying charge $+e$ and an electron in the first equilibrium position.) The first term on the right hand side of equation (5) represents the Coulomb potential, the second the quantum potential.

When an electron has settled down into its equilibrium position the value of W , as follows from equations (3) and (5), becomes —

$$\left. \begin{aligned} W &= \frac{Z^2 W_0}{n^2} \\ W &= \frac{2\pi^2 m e^4 Z^2}{h^2 n^2} \end{aligned} \right\} \quad (7)$$

which is identical with the result obtained by Bohr for the total energy in any stationary state.

If we now consider the shift of an electron from a position where the quantum state of the electron is n to a position where it is n_0 we have —

$$W_{n_0} - W_n = \frac{2\pi^2 m e^4 Z^2}{h^2} \left(\frac{1}{n_0^2} - \frac{1}{n^2} \right) \quad (8)$$

which, if equated to $h\nu$, gives the Balmer series and a value for the Rydberg constant identical with that given by the Bohr theory. "According to the present theory, if the quantum number of an electron in a stable position decreases by one unit, the electron is no longer stable, but falls towards its new position of equilibrium and oscillates about this position. It then radiates its energy of oscillation [equivalent to $h\nu$] according to the usual laws of electrodynamics."¹

Returning to the expression for the quantum force, namely equation (2), it will be observed that it contains the mass m of an electron and so for a given value of n leads to a constant value of F_q whatever the mass of the nucleus may be. It will be recalled that the Rydberg constant as analysed by Bohr is not really constant (and this conclusion is justified by experiment), in that in its exact form it contains the mass of the

¹ If the electron be disturbed from its position of equilibrium it oscillates about this position, retaining its quantum state, say n , unchanged. The frequency of this oscillation ω is given, according to Langmuir, by the expression—

$$\omega = \frac{4\pi^2 Z^2 m e^4}{n^3 h^3}$$

this expression being identical with that obtained by Bohr for the frequency of revolution of an electron in an orbit.

(The above equation could be arrived at by assuming with Bohr that $W = \frac{nh\omega}{2}$

and combining this with equation (7), viz. $W = \frac{2\pi^2 m e^4 Z^2}{h^2 n^2}$. It is difficult to see,

however, the justification for setting $W = \frac{nh\omega}{2}$ in the present case. The expression may be deduced, however, on the basis of the static atom involving the Whittaker model (cf. Allen, *Proc. Phys. Soc.* (1922).)

nucleus M , the term m being replaced by $mM/(M + m)$. A more exact form of equation (2) is therefore—

$$F_q = \left(\frac{nh}{2\pi}\right)^2 \frac{M + m}{Mmr^3} \quad (2a)$$

This result, according to Langmuir, “seems to indicate that the quantum force is due to an interaction between the electron and the nucleus in which both masses play a similar role.”

“Sommerfeld has accounted for the fine line structure of spectral lines by considering a relativity correction due to the rapid motion of the electron [*cf.* Appendix IV.]. This would seem to be excellent proof that the electrons do move. However, it is possible that the motion resides within the electron and nucleus.”

In rejecting the Bohr concept of the revolving electron and substituting positions of stationary equilibrium it is evident that the Lewis-Langmuir atom avoids the chief difficulty pertaining to Bohr's theory, namely, the postulate that an electron when revolving in its orbit neither absorbs nor emits radiation, a postulate at variance with classical electromagnetic theory which require emission or absorption of radiation from an accelerated electron (according as the acceleration is negative or positive) and movement in an orbit constitutes an accelerated type of motion.

In equations (2) or (2a) we have considered the quantum force of repulsion between an electron and a nucleus. The next point to consider would be the quantum force between two electrons. According to Langmuir this may be either attraction or repulsion, according to circumstances, *i.e.* according as to whether the two electrons are on the same side of the nucleus or on opposite sides.

The Whittaker-Ewing Magnetic Model of the Quantum Mechanism in the Atom.

(*Cf.* Whittaker, *Proc. Roy. Soc., Edin.*, **42**, 120 ; Ewing, *ibid.*, 143, 1922.)

The atomic structure here postulated is a system of magnets rigidly connected like the spokes of a wheel, having poles of the same name at the circumference, the corresponding poles of contrary name being all at the centre. According to Whittaker, when a bombarding electron moving in the direction of the axis approaches such a wheel, it sets the wheel turning, the rotation of the poles constituting a “magnetic current”.¹ If the speed of the electron is too low it will be reflected

¹ Although the model here considered is magnetic it is essential to observe that the force contemplated as acting upon the moving electron is electrical in nature. As Whittaker points out: there are two kinds of force which are capable of acting on an electron, namely electric force and magnetic force, and we have to decide which of these two is operative in the present case. The decision is easy, since we know that motion through a field of electric force affects the kinetic energy of an electron, while motion through a field of magnetic force deflects its direction of motion without altering its energy; and in our case the fate of the electron depends entirely on

back without loss of energy, *i.e.* the collision is elastic. If the speed exceeds a certain limit the electron is supposed to pass right through the atomic system and it escapes, but with a definite reduction of velocity, depending on the amount of energy it has given up to the wheel. When the encounter is elastic the angular velocity which the wheel acquires during the approach of the electron is lost during the return of the electron. When the encounter is not elastic and the electron has passed through, the wheel is left with an angular velocity ω ; and the energy which that represents is the source of the radiation emitted subsequently by the atomic system. The energy communicated to the system may be denoted by U , where—

$$U = \frac{1}{2} A \omega^2 = \frac{2e^2 M^2}{A},$$

M being the sum of the magnetic poles at the circumference, A the moment of inertia of the wheel, and e the charge on an electron. The angular momentum communicated to the wheel is—

$$A\omega = 2eM.$$

The electron whose mass is m has its speed reduced from u to v which is such that—

$$U = \frac{1}{2} m(u^2 - v^2).$$

This is the quantum of energy which is related to the frequency of the consequent radiations by the Planck equation—

$$U = h\nu.$$

It follows that the acquired angular momentum on the part of the wheel is given by—

$$A\omega = h \frac{A\nu}{eM},$$

and, since h is a constant of the dimensions of angular momentum, the frequency ν is either equal to eM/A or is a numerical multiple of it. Also since e is constant—

$$\nu \propto M/A.$$

The question now arises as to how the rotational energy $\frac{1}{2} A \omega^2$, which is communicated to the wheel by the bombarding electron, is converted into an oscillatory form, so that the structure will be capable of emitting as radiation the energy which it took up primarily from the passage of the electron through it. Some picture must be formed of this process in order to make the model capable of explaining not

whether it possesses enough kinetic energy to force its way through the field. The field must therefore be electric. A magnetic current such as that envisaged in the model will possess an electric field which will tend to repel the electron, the motion of approach of which in the first instance brought the magnetic current and its electric field into being.

only absorption of energy from matter (electrons) but also capable of emitting and of absorbing radiation directly. Ewing has therefore extended Whittaker's considerations to a somewhat more complex type of magnet model system, such as he had himself already employed. Ewing's treatment is as follows: In the first place, it is evident that Whittaker's model as outlined¹ only goes as far as giving a steady motion in one direction to the wheel, whereas what is wanted is an oscillatory movement corresponding to the emission of a train of waves. To make this possible Ewing envisages an atom as consisting of two parts. The central part, which has been called the wheel, is as described above. The second or outer part of the system likewise consists of magnets as shown in Fig. 13. The outer system of magnets is called the ring (ABCD). Each part is taken as rigid but there is freedom of

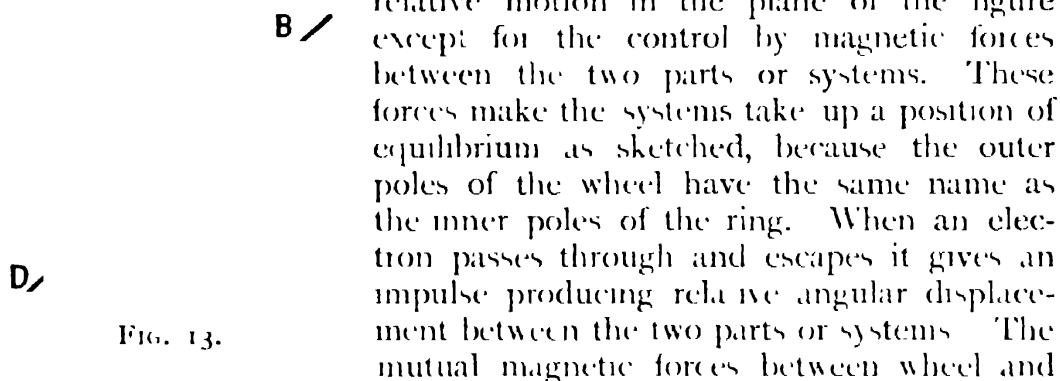


FIG. 13.

relative motion in the plane of the figure except for the control by magnetic forces between the two parts or systems. These forces make the systems take up a position of equilibrium as sketched, because the outer poles of the wheel have the same name as the inner poles of the ring. When an electron passes through and escapes it gives an impulse producing relative angular displacement between the two parts or systems. The mutual magnetic forces between wheel and

ring tend to restore the whole to its original configuration. Thus oscillations are set up which expend the energy in the emitted radiation. It will be observed that on the basis of the above model the electron gives angular momentum to the atom at the expense of a part of its own linear momentum. This is an example therefore of the conversion of linear momentum into angular. When an electron is emitted from an atom it must give an angular impulse to the atom which it leaves. This has a bearing on photo-electricity. We may imagine the magnetic system of the atom to be thrown into oscillation by resonance as a result of the incidence of light of appropriate wave-length, and when the amplitude reaches a certain limit an electron is ejected. In being ejected it exerts an angular impulse which stops the oscillation and deprives the atom of the quantum of energy which has been absorbed through resonance.

The Balmer Series and Rydberg Constant on the Basis of the Whittaker-Ewing model.

This exceedingly important aspect of the magnetic model has been investigated more particularly by H. S. Allen (*Proc. Roy. Soc. Edin.*, **42**, 213, 1922; also *Proc. Phys. Soc.*, **34**, 198, 1922)

Considering the case of the magnetic wheel, radius a , rotating about

¹ Whittaker himself (*loc. cit.*) has extended his considerations to emission of radiation by introducing the concept of a Hertz oscillator.

its axis with an angular velocity $\dot{\psi}$, it follows that the wheel sets up an electric field such that an electron (charge e , mass m) situated at a point on the axis at a distance x from the centre of the wheel is acted on by a force $Mea^2\dot{\psi}/(a^2 + x^2)^{3/2}$ along the axis, where M has already been defined as the sum of the magnet poles (of one sign) in the wheel. Suppose that $\dot{\psi}$ has reached a limiting value ω , i.e. the wheel possesses just one quantum of energy of a certain frequency, and suppose that the electron is situated at a point sufficiently far from the wheel (distance r) that $x = r$ is large compared to a , then the force due to the wheel acting on the electron is $Mea^2\omega/r^3$. When the wheel is in the condition just referred to its angular momentum has attained a certain quantum value or state, given by—

$$A\omega = 2eM = nh/2\pi.$$

(This quantisation of angular momentum, as has already been pointed out earlier in this chapter, is the essence of the application of quantum considerations at all to atomic structure, and is common to all types of atomic structure that are physically possible.)

Combining the two above expressions and eliminating M it is found that the force exerted by the wheel on the electron *under the above conditions* is—

$$\text{force} = \frac{a^2}{2Ar^3} \left(\frac{nh}{2\pi} \right)^2$$

This is the result obtained by Allen, who further points out that it is *identical with the quantum force expression of Langmuir* (cf. earlier section of this chapter) *for a position of equilibrium of an electron in a static atom*, namely—

$$F_a = \frac{1}{r^3} \left(\frac{nh}{2\pi} \right)^2$$

provided A (the moment of inertia of the wheel) can be identified with $\frac{1}{2}ma^2$.

“This might be taken to indicate that the moment of inertia of the magnetic wheel is the same as would be obtained by imagining a mass equal to that of an electron distributed uniformly over a circular disc of radius a . It must, however, be remembered that we are to regard the inertia of the magnetic structure as located in the electro-magnetic field.”

The above considerations are of importance in that they afford a possible physical basis for Langmuir's quantum force expression, which in turn allows of the Lewis-Langmuir atomic model being employed to obtain several of the most striking *physical* results (notably the Balmer series expression and the Rydberg constant), which hitherto had been obtained on the basis of Bohr's model alone.

It will be noted that it is implied in Allen's treatment that the magnetic wheel is located in the nucleus of the atom.

If it be permissible to regard the wheel as the true oscillator, in the sense of Planck's *third* formulation of the quantum theory (cf. Chap. II.),

it would be necessary to assume that an electron in the atomic atmosphere possesses energy in virtue of having at some period in its existence passed through the nucleus and thus abstracted energy from it.

Naturally the concept of a magnetic wheel consisting of a number of very small bar magnets is not intended to actually represent physical structure. Allen (*loc. cit.*) replaces it by two thin anchor rings, "representing the magnetons either of McLaren or of Parson, placed near together with their planes parallel and having a common axis. To obtain the required distribution of the lines of magnetic force the rings must be placed so that the magnetic force between them is one of repulsion. Such an arrangement is equivalent to a magnetic shell forming the curved surface of a cylinder having its edges coincident with the two rings. It is of interest to consider what modifications are required in Prof. Whittaker's equations if we substitute such a magnetic shell for his magnetic wheel. If ϕ denote the strength of the shell and d the distance between the two rings, I find that [in Whittaker's equations] the quantity M must be replaced by $2\pi\phi d$. If we prefer to think of two ring electrons with currents circulating round them in opposite directions, ϕ is proportional to the strength of the current in each ring."

•

--Selective photo-electric effect.

VAPORISATION AND SUBLIMATION.

We have already seen (Vol. II) that thermodynamics leads to a relationship between the latent heat of vaporisation or sublimation and the pressure of the saturated vapour, namely Clapeyron's equation. This necessarily refers to equilibrium conditions and gives us no information about the act of vaporisation itself. In the latter connection the most important quantity is the rate of vaporisation, which may be defined as the mass of vapour which leaves unit area of the liquid in unit time.

This quantity depends on a variety of conditions. These have been examined by various investigators, e.g. H. Hertz (*Ann. Physik*, **17**, 177, 1882); Stefan (*Ib.*, p. 550); Knudsen (*Ib.*, **47**, 697, 1915); Langmuir (*Phys. Rev.*, **2**, 331, 1913); Burger (*Proc. Acad. Wetenschap. Amsterdam*, **21**, 1917). Let us consider the case in which the vapour is saturated. It has already been pointed out (*cf.* Vol. I, Chap. X.) that the rate at which the vapour molecules strike unit area of surface per second is given by,—

$$m = \sqrt{\frac{M}{2\pi RT}} \times p \quad . \quad (1)$$

where m is expressed in grams of vapour, M the molecular weight of the vapour, R the gas constant per grammolecule and p the vapour pressure. If all the molecules, represented by m , condense, it follows that equation (1) gives the rate of vaporisation required to maintain equilibrium.

The question as to whether the molecules represented by m in equation (1) condense or are reflected has been examined by Knudsen (*loc. cit.*), by Langmuir (Vol. I, Chap. X.), and by Volmer and Estermann (*Zeitsch. Physik*, **7**, 1-12, 1921; *Zeitsch. physikal. Chem.*, **93**, 383, 1921). For the case of mercury, Knudsen found that α , the fraction condensed, was 0.95 at 19.45° C., and $\alpha = 1$ at -140° C. Volmer and Estermann have determined the values of α over the temperature range +59° to -64° C., and have found that for the act of condensation on liquid mercury α is unity, and consequently equation (1) is quantitatively correct for this case. For solid mercury $\alpha = 0.9$. The ratio,

α (solid)/ α (liquid), has been determined for sulphur, phosphorus, and benzophenone, and the values 0.3 – 0.4, 0.4 – 0.5, and 0.25 respectively have been obtained. The lower the temperature in the case of a solid the lower is the value of α . There is a close connection between the value of α and the extent to which the liquid can be supercooled.

The effect of temperature on the rate of vaporisation can be obtained by introducing Clapeyron's equation, according to which

$$\frac{d \log p}{dT} = \frac{L}{RT^2}$$

where L is the latent heat of vaporisation per gram-molecule. L can be written as $L_i + RT$, where L_i is the internal latent heat of vaporisation. The gas law is assumed for the vapour. Denoting the concentration of the saturated vapour by C we then have—

$$\frac{d \log C}{dT} = \frac{L_i}{RT^2}$$

or

$$C = C_0 e^{-L_i/RT}$$

assuming as an approximation that L_i is independent of temperature. Equation (1) may also be written—

$$m = \sqrt{\frac{MRT}{2\pi}} \times C.$$

On substituting the above value for C we obtain—

$$m = \sqrt{\frac{MRT}{2\pi}} \times C_0 \cdot e^{-L_i/RT} \quad (2)$$

This equation shows that m varies in a somewhat complicated way with the temperature, but mainly as an exponential function, the actual rate being defined in large measure by the value of the energy term, L_i .

The act of vaporisation and of sublimation has been quantised by Perrin in his essay "Matière et Lumière" (*Annales de Physique* [ix.], **11**, 5-108 (1919)) by writing—

$$L_i = Nh\nu,$$

where N is the Avogadro number, h Planck's constant, and ν the frequency of the radiation (infra-red radiation) which is supposed to cause the rupture of the molecule from its neighbours in the liquid state. This expression, as Perrin is careful to point out, is a simplified form of a more general one involving the difference of two frequencies, *viz.*—

$$L_i = Nh(\nu - \nu')$$

where ν' refers to the vapour molecules, and, for the process considered, is regarded as negligible compared with ν . This expression will be more readily understood when the reader has familiarised himself with the

applications which have been made of quantum considerations to ordinary or thermal reactions in general (*cf.* Chap. VII.).

It is essential in this connection to observe that in the act of vaporisation or sublimation we are dealing with a thermal phenomenon, *i.e.* one that is due to the temperature of the system. As will be seen in Chapter VII., this means that if absorption of radiation is the cause of such changes, the radiation must be conceived of as being in equilibrium with the matter, that is, both are at the same temperature. The phenomenon of vaporisation or sublimation is in fact completely analogous to the phenomenon of thermionic emission (*vide infra*). If it were possible to cause detachment of the molecules from the surface of a liquid by exposing the surface to radiation from an external source, *i.e.* high temperature radiation of frequency ν , the effect would no longer be governed by equations (1) and (2), but would be analogous to the photo-electric effect (*vide infra*). Since the magnitude of the photo-electric effect for a given ν is only one-millionth or less in magnitude of the thermionic effect, one may expect the same relative magnitude to hold for vaporisation as ordinarily produced on the one hand, and as hypothetically produced by external radiation on the other. That vaporisation can be brought about by exposure to high temperature radiation is well known; the process, however, is regarded as due to general warming up of the surface layers of the liquid and ultimately the whole of the liquid by convection so that the effect produced is essentially a thermal one as distinct from a photo-chemical one.

For many liquids the value of ν required to account for vaporisation corresponds to the short infra-red region, 1 to 6μ . Thus, for mercury, $L_v = 13,500$ cal. per mole (and in this case the quantity is practically independent of temperature between room temperature and 880° C.). This energy term requires that ν shall be about 1.4×10^{14} or $\lambda = 2.14\mu$.

Again, since $L_v = N h \nu$, and $L_v = L - RT = L - 2'T$, it follows that—

$$\nu = \text{constant} \cdot (L - 2'T).$$

But, according to Trouton's rule (Chap. III., Vol. II.), the molar latent heat L is proportional to the absolute boiling point. Hence, as Perrin points out, the above relation shows that the frequency of the radiation which determines the vaporisation is proportional to the boiling point. On this basis the radiation which vaporises liquid hydrogen (boiling point 20 abs.) should have a wave-length of about 70μ , whilst the wave-length for helium (boiling point = 4.4° abs.) should be about 0.3 mm. (The wave-length corresponding to maximum intensity of thermal (black body) radiation at this very low temperature occurs at about 0.66 mm.).

In the case of sublimation Perrin mentions that a wave-length of about 5μ should sublime solid carbonic acid, the corresponding wave-length for camphor being 2.4μ .

In the above method of quantising the act of vaporisation it will be

observed that the necessary energy is regarded as contributed by a single frequency. It is usual to regard vaporisation as due to certain molecules which possess kinetic energy in excess of the average value characteristic of the temperature.

This, however, is not a sufficient explanation of the phenomenon, for, as is shown by the different values of L_v and L_f for different substances, the act of vaporisation depends also on the molecular cohesion characteristic of the liquid in question. It would seem, therefore, that it is the cohesion which has to be quantised, and this *might* be conceived of as involving a characteristic frequency. Further, cohesion tends to give a definite orientation and structure to the liquid, which is being destroyed by the thermal agitation of the molecules. If, however, the act of absorption of radiation were very rapid compared with molecular movement we might regard the molecules of the liquid as momentarily stationary, the system being analogous, therefore, to a solid. This is the view taken by Perrin, who points out that in the case of pentane during the time taken for 200 vibrations of the radiation the molecule has only moved through a distance equal to its own diameter.

The analogy between vaporisation and thermionic emission appears to be so close that the former phenomenon should be viewed in the light of the results so far obtained in the case of the latter (*vide infra*).

Incidentally, the origin of molecular kinetic energy itself is probably to be sought ultimately in terms of radiation, *i.e.* as due to energy communicated in the first place in this form; if this is so it would appear necessary to conclude that all the wave-lengths of temperature—or “full” radiation—participated, and this by implication would lead us to believe that cohesion should be treated in the same manner, though of course this conclusion is by no means rigid.

To obtain information regarding a possible single (or approximately single) frequency responsible for vaporisation from infra-red absorption spectra it would be necessary to compare the spectra of liquid and vapour and to discover if possible a band or bands present in the liquid which are absent in the vapour. Although there are a good many data available in the case of liquids, those for the corresponding saturated vapour are scanty. Bands common to both phases would indicate types of internal motion of which the molecules were capable independent of the physical state.

In the case of water it is known that the vapour is remarkably transparent in the region 9μ to 13μ approximately whilst the liquid is exceedingly opaque in the same region. If, say, 10μ were regarded as corresponding with the act of vaporisation, the value of L_v per mole would be 2832 cal. The experimental value for L_v is about 9000 cal. This, however, is an abnormally large value owing to its including the work necessary to decompose the polymers in liquid water. The value for L_v , if water were a normal unpolymerised liquid, would be approximately 7000 cal. This is nearly three times as great as that inferred from the behaviour of water and its vapour at 10μ . To account for a latent heat of 7000 cal. would require a characteristic

frequency corresponding to a wave-length of about 4μ . In this short infra-red region, water, in both physical states, possesses numerous bands, and it is apparently unknown whether the spectrum of the liquid differs from that of the vapour in this region.

In contradistinction to Perrin's view, Rideal (*Phil. Mag.*, **42**, 156, 1921) regards the process of vaporisation as due to a whole range of frequencies, this being necessitated by the consideration that the internal energy content of molecules (and possibly, therefore, their residual valency properties, which determine cohesion) is distributed at haphazard amongst the molecules so that, whilst some molecules require little or no additional energy to become "activated" with respect to the act of vaporisation, others require much more to reach the same state of activation. The question is, on what does this distribution of energy depend? Rideal assumes that the distribution is governed by the nature of the circumambient radiation—in temperature equilibrium with the matter which it interpenetrates—and consequently follows the law of Planck for the distribution of energy in the normal spectrum. It will be recalled that the latter is a continuous curve passing through a maximum at a particular wave-length which depends on the temperature.

According to this hypothesis the magnitude of the various ordinates in the E, λ curve would be proportional to n/h , where n is the number of molecules each possessing the amount of energy $h\nu$. If substances in their interior possess characteristic spectral features Rideal assumes that there would be a series of such ordinates spaced according to the number of spectral lines; an attractive hypothesis, which requires confirmation, however, in view of what follows. In the case of "black" molecules, "i.e. those capable of all possible reactive frequencies, the curve would naturally be complete, since the ordinates would be contiguous and the conditions obtaining would then coincide with those assumed by Planck for equilibrium in a Hohlraum" or black body space.

If the highest possible boiling point, *i.e.* the critical point, happened to correspond in general to a very high temperature, it would be possible to assume that even with a distribution of energy such as that assumed above that the number of molecules requiring a certain amount of activation (*i.e.* energy values lying between relatively narrow limits) would be so great that the remainder would be negligible. In this sense there would be a most probable frequency (approximately monochromatic) responsible for the vaporisation. But, in view of the relatively low values to be assigned to critical temperatures and in view of the fact that vaporisation takes place at the lowest temperatures, the above approximation regarding monochromatism would appear to be inadmissible, since the E, λ curve is very flat at low temperatures, and, if Rideal's initial assumption is correct, integration over a wide range would be required.

We have now to consider an interesting relation pointed out by Rideal in connection with Trouton's rule.

At their critical temperatures T_c all substances are in corresponding states, the value of L being zero. That is, at the critical temperatures all the molecules of different substances are activated with respect to the act of vaporisation. Rideal concludes, on the basis of the assumption made above, that critical temperatures are corresponding temperatures likewise in respect of distribution of internal energy among the molecules in the interior of substances, *i.e.*, that at the critical temperature the E, λ curves for different substances can be superimposed. For the Hohlraum, Wien's Displacement Law states that, $\lambda_{\max.} \times T = \text{constant}$, where $\lambda_{\max.}$ is the wave-length corresponding to a maximum value of the radiational energy density or intensity. Transferring this idea to the conditions postulated as obtaining in the interior of different substances we can write: $\lambda_{\max.} \times T_c = \text{constant}$, where the constant is independent of the substance considered. This is equivalent to writing $T_c/\nu_{\max.} = \text{constant}$ or $T_c/Nh\nu_{\max.} = \text{constant}$. If now the molar latent heat L be identified¹ with $Nh\nu_{\max.}$ we obtain $T_c/L = \text{constant}$, or $L/T_c = \text{constant}$. This is the more exact formulation of Trouton's rule,² which, according to Rideal, is directly connected, therefore, with Wien's Displacement Law. The difficulty is that the assumption that $Nh\nu_{\max.} = L$ is a return to Perrin's idea of a single frequency and is opposed to the initial postulate which requires that L , or better L_v , should be represented by a sum of terms $\Sigma h\nu$. The remarkable thing, however, is, as Rideal shows, that not only is there an analogy between Wien's Displacement Law and Trouton's rule, but that the constant is identical in the two expressions. Experiment has shown that the value of $\lambda_{\max.} \times T$ for a Hohlraum is 0.28986 when λ is measured in cms. Inserting the numerical values for N and h it is found that :

$$L = 9.866 T_c$$

where L is measured in cal. per mole. The value of the constant 9.866 lies between the value given by Trouton's rule, namely 14.66, and the value given by van der Waal's equation, namely 7.2.

The above conclusion has been compared by Rideal with the experimental values. The data are given in the following table. "It will be noted that for the simple molecules [*i.e.* those in which work of depolymerisation is not required] the Wien constant value for the latent of evaporation agrees more closely with the experimentally derived values than that of Trouton, with the more complex molecules, on the other hand, the Wien constant values agree remarkably closely with the values of the latent heat calculated from the critical data of van der Waals' equation, but are below those experimentally determined with which Trouton's calculations coincide."

¹ L is employed here although it would be more correct to employ L_v .

² Trouton's rule states that $L/T_b = (\text{an approximate}) \text{ constant} = 22 \text{ cal.}$, where T_b is the boiling point on the absolute scale. The boiling points are approximately two-thirds of the critical temperatures, and it is found experimentally that $L/T_c = 22 \times \frac{2}{3} = 14.66$ holds better than the original form of the rule.

Substance	Critical Temp. T_c	L. Calc. from Wien's Law.	L. Calc. from van der Waals' Expression.	L. Calc. from Trouton Rule	L. Calc. from Vapour-pressure Data or Experimental Data.
He . . .	5.0	49.33		88.2	49.3
Ar . . .	155.0	1529		1827	1501
Hg . . .	1350	13,340		13,200	14,500
N ₂ . . .	127	1253		1623	1362
O ₂ . . .	155	1529		1890	1599
H ₂ . . .	31	306		420	250
CO . . .	132	1302		1743	1414
CO ₂ . . .	304	3000		4095	3200
Cl ₂ . . .	419	4144		5027	4000
Br ₂ . . .	575	5590		7056	7200
I ₂ . . .	785	7740			7590
CS ₂ . . .	550	5426	5300	4769	6490
SO ₂ . . .	429	4233	4200	5523	5837
CCl ₃ H . . .	541	5330	5400	6993	6900
C ₆ H ₆ . . .	561.5	5540	5400	7413	7240
C ₆ H ₁₂ . . .	468	4616	—	6384	6000
C ₆ H ₅ .NH ₂ . . .	698.6	6892	7100	9597	9672
Et. O. Et . . .	470	4638	4600	6468	6260
Et. OH . . .	516	5091	5640	7378	9448
H ₂ O . . .	645	6364	8800	7883	9660
CH ₃ COOH . . .	594.6	5866	8500	8110	5400 per mol. or 8370 for associated vapour.

In view of Rideal's application of Wien's Displacement Law to the phenomenon of vaporisation it is of interest to consider the nature of the distribution of internal energy among molecules of different substances at one and the same temperature. Under these conditions it would seem that the E, λ curves for different substances must be of the same type; they must be regular and continuous and exhibit a single maximum. That is, no special characteristics or "bands" apparently manifest themselves in the interior. The energy distribution curves must in fact be similar to (though not identical with) the curve for a Hohlraum at the same temperature. The curves for different substances cannot be superimposed at the same temperature; Rideal assumes that they can be superimposed at the respective critical temperatures, or in fact at any corresponding temperatures. If we compare, say at room temperature, a substance with a low critical temperature with a substance having a high critical temperature we would say that the first body has a greater fraction of activated molecules (*i.e.* activated with respect to vaporisation) than the second. The absence of all specific characteristics analogous to bands is at first sight incompatible with the well-known specific nature of emission and absorption spectra. To make them compatible it would be necessary to assume that such specific characteristics tend to manifest themselves in the interior but they are obliterated by the rapid transformations of energy due to reflections, absorptions and emissions on the part of the molecules composing the matter, such transformations being the *modus operandi* whereby the matter and the radiation interpenetrating it are

maintained at the same temperature. The specific characteristics on this view are observable only when the temperature of the radiation to which the matter is exposed is not the same as that of the matter itself.

Rideal's application of Wien's Displacement Law also raises the question of the part played by Wien's second expression, *viz.* $E_{\max.}/T^5 = \text{constant}$.

The foregoing outline indicates the position of the problem of quantisation of vaporisation and sublimation at the present time (1923). Evidently the treatment is of a preliminary character only. In the first place, since the quantum theory as developed by Planck does not permit of the frequency varying as a function of temperature, it is clear that in any attempt at an exact quantisation it is necessary to separate out the variable from the constant parts in any energy term. The internal latent heat varies with the temperature fairly rapidly in that it becomes zero at the critical point. This variation, it may be pointed out, is much greater than that met with in the analogous term in true chemical change. We can write—

$$L_0 + \int_0^1 \frac{\partial L_1}{\partial T} dT$$

where $\frac{\partial L_1}{\partial T}$ is taken account of by the specific heats of vapour and liquid.

The latter terms themselves require separate quantisation, but, whilst this has been done to a certain extent in the case of gases (*cf.* Chap. IV), practically nothing has been done in this direction for liquids. The term L_0 is the truly constant part in the vaporisation term and it is this quantity which should be considered in connection with the still unsolved problem as to whether a single frequency or a whole group of frequencies is required. Rideal's semi-empirical relation, involving Wien's Displacement Law, seems to suggest the employment of a single frequency even though there is black body distribution of radiation and internal energy throughout the molecules of the system at the same time. The quantum equation for radiation density as a function of wave-length in a Hohlraum has been extended by Planck himself to include a Hohlraum in which the refractive index is not unity but has the value n . Whether this makes it applicable to the interior of actual matter is a problem of the first importance, as it bears not only on vapourisation but on chemical change as well. If in the interior of matter there are regions of enhancement of the E, λ curve so that not one but several maxima exist, Planck's equation would appear to be inapplicable and Wien's Displacement Law meaningless. Rideal's investigation seems to point, however, to a greater similarity between different substances and the Hohlraum itself than would otherwise have been anticipated.

Fusion.

Consider the case of a monatomic solid. Its energy consists, as we have seen (Chap. III.), of atomic vibrations. On the equipartition view this energy would amount to $3RT$ per gram-atom, one half being

kinetic the other potential energy. On the quantum theory this expression is replaced, say, by that of Debye and may be represented by $3Rf(\theta_1/T)$ where $f(\theta_1/T)$ is the Debye function, θ_1 being the "characteristic temperature" of the substance in question.

As a result of the mutual attractions and repulsions of the atoms in a solid, they form a space lattice, which is regular in the case of crystalline substances, irregular in the case of amorphous solids. At low temperatures the restoring force on an atom is taken to be proportional to the displacement, giving rise to simple harmonic vibratory motion in which the potential energy is on the average equal to the kinetic. As the melting point is approached, the amplitude of the atomic vibrations increases until the atoms interfere with one another—*cf.* Lindemann's melting-point method of obtaining the characteristic frequency of a solid (Chap. III)—presumably as a result of the overlapping of their outermost electronic orbits. As a consequence of this a crystalline solid loses its crystalline form and melts sharply. Under such conditions the potential energy may exceed the kinetic. Monatomic solids expand on fusion, and, according to Lindemann (*Phil. Mag.*, **45**, 1120, 1923), about one half of the latent heat of fusion is due to the work required to overcome cohesion. "On account of the greater distance between the atoms in the liquid, the restoring force is less than in the solid and consequently the atom's frequency and the 'characteristic temperature' θ_2 must be lower. The balance of the latent heat is therefore probably accounted for by the term—

$$3R \int_{\theta_2}^{\theta_1} (f(\theta_1/T) - f(\theta_2/T)) dT."$$

It should be mentioned that Perrin (*loc. cit.*) treats the process of fusion and crystallisation from precisely the same point of view as that adopted by him in connection with the process of vaporisation (*q.v.*).

THERMIONIC EMISSION ("THERMIONICS").

By the term thermionics is meant the emission of *electrons* from heated solids due to the temperature of the latter. The emission is due therefore ultimately to the radiant energy interpenetrating the solid, in virtue of which the various atoms or molecules composing it possess a certain distribution of potential and kinetic energy, which distribution of energy content permits us to assign a certain temperature to the solid. The emission of electrons varies rapidly with the temperature, so that although at ordinary temperatures such emission is too small to be detected it becomes sensible at higher temperatures.

Thermionic emission is to be clearly distinguished from the photo-electric effect, or emission of electrons from the surface of a solid owing to the exposure of the surface to an external source of radiation, usually of short wave-length. Under the latter (photo-electric) conditions, the emission is not connected with the temperature of the solid at all, but depends essentially upon the choice and intensity of the impinging

light. The term "auto-photo-electric emission" will be used later in connection with thermionics. This has to be distinguished from the ordinary use of the term photo-electric. The auto-effect depends essentially upon the radiation interpenetrating the matter in virtue of the temperature of the matter. It is convenient to group together in one's mind the two phenomena of thermionics and ordinary thermal reactions, both having their origin in what gives temperature to the system. On the other hand, we have to group together photo-electric effects and photo-chemical action (as ordinarily understood) in that both are due to impinging external radiation usually possessing a temperature which is high compared with that of the matter upon which the radiation acts.

Our knowledge of the subject of thermionics is due principally to O. W. Richardson and his collaborators.¹ The most characteristic features of the phenomenon may be thus summarised:—

1. The number of electrons n emitted at any temperature T is given by an expression of the form:—

$$n = AT^{\lambda}e^{-b/T}$$

where A , λ and b are constants. λ is of the order unity, its most probable value being $1/2$. The term b can be written as w/R where R is the gas constant per gram-molecule and w is an energy term the value of which usually lies between 30,000 and 50,000 calories. The deduction of the above equation will be given later.

2. The emission of electrons is accompanied by an absorption of heat of a magnitude in general agreement with the value ascribed to b . Similarly the absorption of electrons by a cold metal is accompanied by an evolution of heat, the value likewise being in agreement with that inferred from the value of b .

3. The energy of the emitted electrons, as well as the distribution of velocity amongst them, is identical with that given by Maxwell's law for molecules possessing the mass of an electron at the same temperature as the emitting metal. It is this fact which demonstrates that thermionic emission is a pure temperature effect. It is also now accepted—the objections will be referred to later—that the emission is a definite property of the metal and is not to be ascribed to chemical change due to accidental impurities. It may, however, be regarded as typifying the simplest possible kind of chemical change in the metal itself if we take it as representing the dissociation of a neutral atom into a positive residue and an electron.

The thermionic emission may be taken as a manifestation of the fact that as the temperature rises the kinetic energy of certain of the electrons begins to exceed the work required to overcome the forces retaining them in their original positions in the solid.

Deduction of Richardson's Thermionic Equation.

The following is the deduction as given by Langmuir (*Trans. Amer. Electrochem. Soc.*, **39**, 125, 1916).

¹ A detailed account will be found for example in Richardson's book: *Emission of Electricity from Hot Bodies*, Longmans.

According to Richardson the distribution of velocities among the electrons which are emitted by a heated metal is given by Maxwell's law,

$$dN = \frac{N}{\sqrt{\pi}} e^{-x^2} dx \quad (1)$$

where N is the number of electrons in each c.c. of the metal, dN the number per c.c. which have velocity components in a given direction lying between v and $v + dv$. The variable x is proportional to v and is given by :—

$$x = \sqrt{\frac{3}{2}} \cdot \frac{v}{\bar{v}} \quad (2)$$

where $\bar{v}$ is the square root of the mean square velocity of the electrons. $\bar{v}$, on the basis of the kinetic theory, is given by :—

$$\bar{v} = \sqrt{\frac{3RT}{M}} \quad (3)$$

where R is the gas constant per gram-molecule and M is the “molecular weight” of an electron (*viz.* 0.000546, oxygen = 16). From (2) and (3) we obtain :—

$$x^2 = \frac{1}{2} M v^2 / RT \quad (4)$$

Richardson assumes a force at the surface of the metal tending to hold the electrons within the metal. In order to escape, an electron must do work against this force. Suppose w is the work which must be done by one gram-molecule, *i.e.* 6.1×10^{23} electrons. The electrons are able to do this in virtue of their kinetic energy. Let v_0 be the smallest velocity component perpendicular to the surface of the metal which an electron must possess in order just to escape. Then,

$$\frac{1}{2} M v_0^2 = w \quad (5)$$

The number of electrons dn with velocity components between v and $v + dv$ which reach a square cm. of the surface per second can be obtained by multiplying the number per c.c. having this velocity by the velocity component. That is, from (1) and (4)—

$$dn = v dN = N \sqrt{\frac{2RT}{\pi M}} \cdot x \cdot e^{-x^2} dx \quad (6)$$

The total number of electrons which reach the surface with a velocity perpendicular to it exceeding v_0 is therefore—

$$n = N \sqrt{\frac{2RT}{\pi M}} \cdot \int_{x_0}^{\infty} e^{-x^2} \cdot x \cdot dx = N \sqrt{\frac{RT}{2\pi M}} \cdot e^{-x_0^2} \quad (7)$$

where $x_0^2 = \frac{\frac{1}{2} M v_0^2}{RT}$ (8)

Combining (5), (7) and (8) we obtain finally:—

$$n = N \sqrt{\frac{RT}{2\pi M}} \cdot e^{-w/RT} \quad (9)$$

This is Richardson's thermionic equation.

The above expression assumes obviously that the thermionic emission is an intrinsic property of the metal.

Further, if a positive field is maintained outside the metal by bringing an electrode (anode) charged to a sufficiently high *positive* potential near to the metallic surface, none of the electrons which have been emitted by the hot metal will return to it. A thermionic *current* will be produced, and evidently if the positive potential of the electrode is sufficiently high to prevent all the electrons from returning to the heated metal a *saturation current* will be attained, independent of any higher potential applied to the electrode. The saturation current i is proportional to n and should therefore be given by equation (9). If we assume that N and w are independent of temperature, equation (9) may be written—

$$i = a \sqrt{T} e^{-b/T} \quad (10)$$

which is the actual type of equation tested experimentally by Richardson. a and b are constants.

Discussion of Richardson's Equation.

Equation (9) (or its equivalent (10)) has been the subject of considerable criticism, but it is now regarded as correct and applicable if the metal surface is really clean. As a result of experimental work carried out under very high vacua (the pressure being less than 10^{-7} mm. of mercury), and every care being taken to eliminate impurities, Langmuir has found that the thermionic emission is an intrinsic property of pure metals and is given by an expression of the above form. As an illustration of the care which must be exercised in work of this kind Langmuir states that oxygen or water vapour even at as low a pressure as 10^{-9} mm. of mercury *diminishes* the electron emission from tungsten materially. CO , CO_2 , and CH_4 decrease the emission slightly; H_2 , mercury vapour, and the inert gases, when pure, are without effect. As the vacuum is improved, the emission in general increases, but reaches a definite limit, which is not changed by further improvement of the vacuum.

As already mentioned, one of the criticisms levelled at Richardson's concept of thermionic emission as an intrinsic property was that the effects observed could be ascribed to chemical action due to an impurity at or in the metal, e.g. adsorbed gases. Langmuir has found, however, that the gases which react most vigorously with tungsten are also those which most markedly *diminish* the thermionic effect. The presence of thorium in tungsten sufficient to give rise to a surface layer

of thorium one atom in depth increases the emission ten-thousand fold.¹ This layer, however, can be distilled off by heating the filament to 2700° , and the emission thereafter corresponds to that of pure tungsten. Langmuir (*loc. cit.*) gives other evidence to show that thermionic emission can be observed with an absolutely pure metal.

In the following table are given some results obtained in Langmuir's laboratory, the result for platinum being an approximate one obtained by Schlichter. The a and b values are the constants in Richardson's equation (10). On comparing (10) with (9) we see that $b = w/R$, where w is the work done when one gram-molecule of electrons escape. Since the amount of current involved in this is one faraday (F), it follows that $w = \Phi F$, or $\Phi = w/F = Rb/F = 8.62 \times 10^{-5} b$ volts, where Φ is an *imaginary*² p.d. exerted at the surface, just sufficient in magnitude to prevent emission; that is, a p.d. which is equivalent in its effect to the forces holding the electrons in the metal. The term $i_{2000^{\circ}}$ denotes the saturation current per cm.² at 2000° absolute.

Metal	a amps per cm ²	b Calories	i_{2000} amps. per cm ²	Φ in Volts
Tungsten	2.36×10^7	52,500	0.0042	4.52
Thorium .	2.0×10^8	39,000	30.0	3.36
Tantalum	1.12×10^7	50,000	0.007	4.31
Molybdenum	2.1×10^7	50,000	0.013	4.31
Carbon .	—	48,000	—	4.14
Titanium	1300	28,000	0.048	2.4 ?
Iron .	2400	37,000	0.001	3.2 ?
Platinum .	1.25×10^7	51,060	0.0035	4.4

The following values of Φ are added for the sake of completeness. Some of them are far from being exact. They have been obtained from the photo-electric effect. As will be pointed out later, Millikan has shown that pure freshly-cut surfaces of metals exhibit best the photo-electric effect. This effect is likewise an intrinsic property of the metal.

Φ in Volts.	Metal
Copper	4.1
Bismuth	3.7
Tin	3.5
Zinc	3.4
Aluminium	2.8
Magnesium	3.2
Lithium	2.35
Sodium	(2.1), 1.82

From the "chemical" point of view we may regard the values attributed to Φ as a measure of the affinity of the metals for electrons.

¹ This result suggests that any phenomenon depending on surface electrical effects—possibly certain types of catalysis—would be largely influenced by a trace of thorium.

² The sense in which the term imaginary is here employed is explained in the section dealing with contact p.d's.

It will be observed that it requires much less work to eject an electron from the alkali metals than is required in the case of, say, platinum or tungsten. Even at relatively low temperatures—300° to 400° C.—electron emission from potassium, in a good vacuum, is large.

We have now to return to a consideration of the probable cause of the whole phenomenon of thermionic emission, that is, the source of the necessary energy. Richardson deals with the problem as follows (British Assoc. Report, 1921):—

“Since the formula for the radiation emitted by a body at any given temperature contains every wave-length without limitation, there must be some emission of electrons from an incandescent body as the result of the auto-photo-electric effect of its own luminosity. Two questions obviously put themselves. Will this [auto] photo-electric emission, caused by the whole spectrum of the black body, vary, as the temperature of the incandescent body is raised, in the way which is known to characterise thermionic emission?” The answer to this question is definitely in the affirmative. “Thus the auto-photo-electric emission has the correct behaviour to account for thermionic emission. The other question is: is it large enough? This is a question of fact. . . . There seems no escape from the conclusion that *the auto-photo-electric effect of the whole spectrum is far too small to account for thermionic emission.*”

This is the outstanding difficulty in interpreting the phenomenon of thermionic emission. It is highly interesting and suggestive that precisely the same difficulty is encountered in the case of ordinary or thermal chemical reactions which proceed in virtue of the temperature of the system. The cause of the discrepancy is undoubtedly the same in the two cases. In the case of chemical reactions, that is, *unimolecular* reactions, which are of course the nearest analogue to thermionic effects, the observed velocity constant is about 2×10^7 times as great as that calculated from the Planck expression for the rate of absorption of radiational energy by an oscillator. This is discussed in Chapter VII.

THERMIONICS AND THE CONTACT POTENTIAL DIFFERENCES BETWEEN METALS.

In the thermodynamic treatment of the electromotive force of cells, as given in Vol. II., Chapter VII., nothing has been said of the possible potential differences existing at the points of contact of unlike metals in the circuits. As regards concentration cells, and gravity and centrifugal cells, in which both electrodes in any cell are of the same kind, it is evident that contact effects, if they exist, mutually cancel. In certain cases, however, such as the Daniell cell, the two electrodes consist of different metals, *e.g.* copper and zinc. In such instances, if there is a real p.d. at the point of contact of the two pure metals—whether this contact is direct or *via* some other metal is immaterial—the question arises as to whether the contact effect has to be allowed for in estimating the correct E.M.F. due to the chemical process occurring in the cell.

The question of the existence or non-existence of such contact

potentials between metals has been under discussion since the time of the first observations of Volta (1797), that a p.d. seemed to exist between zinc and copper, the copper being negatively charged with respect to the zinc, which effect Volta attributed to "contact action". As investigation proceeded, stress was laid more and more on the chemical process occurring in the cell, so that it came to be generally believed that contact action as such did not exist; that when such effects were observed, as in Volta's original experiments, these were due to a film of moisture between the metals, and were in fact evidence for the chemical origin of the p.d. as opposed to the "contact" origin. This conclusion appeared to be very strongly supported by the experiments of J. Brown, who showed that if two dissimilar metals are boiled in oil so as to remove moisture, no p.d. manifests itself when the metals are brought into contact. The criticism that a non-conducting layer of oil was left between the metals and could not produce any electrical effects seems scarcely to have been considered.

The whole question of the existence of a contact p.d. has been raised, however, by the modern work on thermionic emission, photo-electric effects, and ionisation potentials (*cf.* in particular, I. Langmuir, *Trans. Amer. Electrochem. Soc.*, **39**, 125, 1916).¹ The evidence collected appears to be sufficiently convincing to demonstrate the real existence of the contact effect. In view of the importance of this conclusion it is necessary to give one of the principal arguments put forward by Richardson in connection with it.

"Imagine a vacuum enclosure, either impervious to heat or maintained at a constant temperature. Let the enclosure contain two different electron-emitting bodies, A and B [emitting in virtue of their common temperature]. Let one of these, say A, have the power of emitting electrons faster than the other, B. Since they are each receiving as well as emitting electrons, A will acquire a positive and B a negative charge under these circumstances. Owing to these opposite charges, A and B will now attract each other, and useful work can be obtained by letting them come into contact. After the charges on A and B have been discharged by bringing them into contact, let the bodies be quickly separated and moved to their original positions. This need involve no expenditure of work as the charges arising from the thermionic emission will not have had time to develop. After the charges have had time to develop, the bodies can again be permitted to move together under their mutual attraction, and so the cycle can be continued an indefinite number of times. In this way we have succeeded in imagining a device which will convert all the heat energy from a source at a uniform temperature into useful work. Now the existence of such a device would contravene the second law of thermodynamics."

There is evidently a fallacy therefore in some one of the assumptions made in the above process. It is necessary, in fact, to modify the alleged behaviour of A and B in order that no useful work on the whole

¹ Ionisation potentials are considered in the following chapter.

may be done. "There are two alternatives. Either A and B necessarily emit equal numbers of electrons at all temperatures, or the charges which develop owing to the unequal rate of emission are not discharged, even to the slightest degree, when the two bodies are placed in contact.

The first alternative is definitely excluded by the experimental evidence." We must fall back therefore on the second. "It means that bodies have natural states of electrification whereby they become charged to definite potential differences whose magnitudes are independent of their relative positions. There is an intrinsic potential difference between A and B which is the same, at a given temperature, whether they are at a distance apart or in contact. In the words of Volta, 'the metals can by themselves and of their own proper virtue excite and dislodge the electric fluid from its state of rest'. Admitting that the intrinsic potentials exist, a straightforward calculation shows that they are intimately connected with the magnitudes of the thermionic emission at a given temperature."

The calculation referred to will be given later. Before doing so, however, it is necessary to distinguish between two electrical quantities, both of them characteristic of metallic conductors, namely the true contact effect discussed above, and the well-known thermo-electric effect of Peltier which forms the basis of temperature measurement by means of thermo-electric couples.

The Peltier effect is in general a small quantity, much smaller than the value ascribed to the true contact p.d. In fact, Helmholtz and Lord Kelvin have regarded the Peltier effect as being related, not to the contact p.d. itself, but to the variation of this p.d. with temperature, the relation being—

$$V_p = T \frac{dV_c}{dT}$$

where V_c is the contact p.d. between two metals at the temperature T , and V_p is the Peltier electromotive force, that is the E.M.F. which is equivalent to the observed absorption or evolution of heat at the junction.

The calculation referred to above, which concerns V_c directly and V_p only indirectly, may now be given (*cf. Science Progress*, **16**, 365, 1922.) The calculation deals mainly with the significance of the Φ term (already met with in discussing thermionics) for contact potentials.

Consider two metallic bodies placed in a vacuum enclosure maintained at constant temperature T . Let w_1 and w_2 refer to the work functions corresponding to the escape of N_0 electrons through the surfaces of each body respectively, where N_0 is the Avogadro number. Let V_1 and V_2 be the potentials in the space *just outside* the surfaces of the metals. The work required to remove N_0 electrons from the first body, transport them across the space between, and carry them into the second metal is—

$$w_1 + (V_1 - V_2)eN_0 - w_2. \quad "$$

Note that the electronic charge is negative, but e is regarded here as its mere magnitude, *i.e.* as a positive number, so that $(V_1 - V_2)e$ is work done *on* the electron in travelling from the place where the potential is V_1 to the place where it is V_2 . Now, by a well-known result, the above sum of work terms must equal $RT \log N_1/N_2$, where R is the gas constant per gram-molecule, and N_1 and N_2 are the "free" or conduction electrons per c.c., in each metal. Hence—

$$\begin{aligned} V_1 - V_2 &= (w_2 - w_1 + \frac{R}{N_0} \log N_1/N_2)/eN_0 \\ &= \Phi_2 - \Phi_1 + \frac{RT}{N_0 e} \log N_1/N_2. \end{aligned}$$

Suppose now that the two metals are placed in contact, then from the values of electric conductivity and thermo-electric measurements we are justified in assuming that N_1 and N_2 are numbers of the same order of magnitude and the logarithmic term is found to lead to comparatively small E.M.F.'s, of the order of magnitude of those required to account for the Peltier effect. Hence we may rewrite the above relation in the approximately correct form—

$$V_1 - V_2 = \Phi_2 - \Phi_1$$

if the metals have been in contact, whether they remain so or are separated. Hence the contact p.d. of the two metals is thus identified as the difference of their Φ values.

Langmuir (*loc. cit.*) has pointed out that it is not correct to regard Φ as a p.d. in the usual sense of the term. A p.d. is defined as existing between two points when the work done on an element of charge δq in transportation is $V\delta q$, and the transportation of the δq *does not appreciably affect the value of V* . But the mechanism of photo-electric and thermionic emission seems to be such that the work involved by the removal of a small but *finite* amount of charge e is due to the back attraction on the e of its mirror image, *i.e.* its induced charge on the surface of the metal, or the balance of opposite charge left unneutralised by its removal. It can be shown (*cf.* Langmuir, *loc. cit.*), on the law of inverse squares, that the amount involved in removing e from a point which is distant x from the surface to infinity is $e^2/4x$, and that if we assume the law of inverse square to hold down to a distance x_0 , and for nearer distances adopt any plausible hypothesis as to attractive force which does not lead to infinite singularities, then $w = e^2/2x_0$ approximately, *i.e.*,

$$\Phi = e/2x_0.$$

If this equation is tested from the known values of Φ and e , it yields quite reasonable values for x_0 , all of the order 10^{-8} cm., as one would expect from the values of atomic dimensions and distances apart calculated on other grounds. It is interesting to note also that it gives an explanation of the statement by Richardson that the values of Φ for

some elements—such as sodium, potassium and carbon—are inversely proportional to the cube roots of their atomic volumes.

From the values of Φ for different metals, determined by any suitable method, thermionic or photo-electric, we should be able to calculate the contact p.d. between any pair of metals. When $\Phi_2 > \Phi_1$, this means that it is more difficult to abstract an electron from metal (2) than from metal (1). Metal (1) will therefore be at a higher electrostatic potential than metal (2). Referring to the tables of Φ values given in the section on thermionics it will be seen that $\Phi_{\text{copper}} = 4.1$ volts, whilst $\Phi_{\text{zinc}} = 3.4$ volts. That is $\Phi_{\text{copper}} > \Phi_{\text{zinc}}$. Hence when these two metals are in contact the copper will be negatively charged compared with the zinc; which is Volta's original observation. Further, the magnitude of this p.d. will be $4.1 - 3.4 = 0.7$ volt., a considerable magnitude.

We have now to consider the case of the E.M.F. of an electrolytic cell, *e.g.* the Daniell cell. In view of the above results there can be no question but that there is a real contact p.d. of considerable size, namely 0.7 volt, at the point of contact of zinc and copper in the circuit. But the copper and zinc electrodes face one another in the opposite sense in the cell itself, and it has been shown above that the p.d. is the same whether the metals are actually in contact—as they are somewhere in the metallic circuit—or whether they are separated from one another, as they are in the cell itself. It seems probable therefore that the contact p.d. though real cancels itself even in this case. To place the conclusion on a firm foundation it would be necessary to carry out measurements analogous to those of Bredig and Knuppfer (Vol. II., Chap. XII.) for an electrochemical reaction involving metals of a different kind, but at the same time a reaction characterised by an equilibrium point which could be determined by independent analytical means. The Daniell cell reaction cannot be employed for this purpose, since the equilibrium point lies so far over to one side as to be beyond the limits of detection by even the most refined analytical methods. If such a reaction were discovered it would be possible to calculate by means of the van't Hoff isotherm what the E.M.F. due to the chemical reaction should be. The result could then be compared with the observed value.

THE PHOTO-ELECTRIC EFFECT.

Hallwachs, in 1888, was the first to show that a body carrying a charge of negative electricity loses its charge on being exposed to ultra-violet light; on the other hand, a positively charged body is not discharged. Later, Hallwachs and Righi showed, independently, that an insulated metal exposed to ultra-violet light acquires a positive charge. That is to say, negatively charged particles, electrons, are emitted from the metal under the action of ultra-violet light. This phenomenon is known as the photo-electric effect. Certain metals, such as the alkali metals and zinc and aluminium, exhibit this effect even under the influence of ordinary "visible" light, the effect being greatest in the case of the alkali metals. It is essential in all these cases that the

surface should be fresh and clean ; if a layer of oxide forms, the effect is greatly weakened. This is known as photo-electric fatigue.

This emission of electrons is bound up with an absorption of the light. The periodic electric force in the radiation sets the electrons on the surface into more violent vibration, so that some of them are ejected from the metal into the neighbouring space. If v is the velocity possessed by an ejected electron, its kinetic energy is $\frac{1}{2}mv^2$, where m is the mass of the electron. If the surface be charged positively to a potential of V volts, which potential is just able to prevent the escape of the electron, it follows that Ve , where e is the charge on the electron, is just equal to $\frac{1}{2}mv^2$, *i.e.* the kinetic energy which the electron would have had if no potential had existed.

Experiment has shown that the photo-electric effect really comprises two phenomena, *apparently* distinct from one another. These are known as the *normal photo-electric effect* and the *selective photo-electric effect* respectively. We shall consider the normal effect in the first place

NORMAL PHOTO-ELECTRIC EFFECT.

The photo-electric current, produced by the moving electrons which have been set free from the surface, depends upon two factors, (1) the *number* of electrons emitted in unit time, and (2) the *speed* of these electrons. If the intensity of the light be increased, without altering the colour or quality (*i.e.* without altering the vibration frequency), it has been found that the photo-electric effect increases proportionally to this intensity, because the *number* of electrons emitted increases in the same proportion. As long, however, as the frequency of the light is maintained constant, the velocity of the electrons is also constant. On the other hand, working with constant intensity of light but varying the quality or frequency it has been found that, on increasing the frequency of the light, the photo-electric effect increases, because the *speed* of the electrons is now increased. According to Lenard and Ladenburg, when the wave-length is thus shortened (at constant intensity) the velocity of the electrons emitted increases proportionally to the frequency. It is now known that the square of the speed is proportional to the frequency of the incident light. Below a certain wave-length or frequency, known as the threshold wave-length, the normal photo-electric effect is not observable. That is, with wave-lengths longer than a certain value λ_0 —characteristic of the substance under examination—*no* electrons are emitted. Hughes has determined the value of λ_0 for a number of substances, using fresh surfaces, obtained by distillation of the substance *in vacuo*. These values are given in the following table:—

NORMAL PHOTO-ELECTRIC EFFECT. THRESHOLD WAVE-LENGTHS (λ_0).

Substance.	λ_0 .	Substance	λ_0 .
Ca	370 $\mu\mu$	Sb	308 $\mu\mu$
Mg	330	As	236
Cd	314	Se	220
Zn	302	O ₂	135
Pb	312	C (soot)	255-260
Bi	323	"	"

The values obtained by Richardson and Compton with freshly scraped surfaces correspond to somewhat longer wave-lengths than those given.

Starting from the above threshold wave-lengths and diminishing the wave-length, the photo-electric effect increases in virtue of an increase in the velocity of the electrons. According to Richardson and Compton this goes on until a certain limiting value, corresponding to an extremely short wave-length, is attained, beyond which the normal photo-electric effect no longer increases.

The emission of an electron at all by the action of light is a process which it is difficult to reconcile with the ordinary wave theory of light, which involves a spreading out of the light and consequent uniform diminution in intensity as we proceed from the source.¹ Yet (*vide supra*) it has been found by Lenard (*Ann. Physik*, iv., **8**, 149, 1902) and verified by Millikan (*Physical Rev.*, **1**, 73, 1913) that the speed and consequently the kinetic energy of electrons ejected is quite independent of the intensity of the light, provided only that its frequency be kept constant. The change in the intensity here referred to may be brought about, for example, by altering the distance of the light-source or by introducing absorbing screens. Further, as already mentioned, on keeping the intensity of the light constant and varying its quality (*i.e.* its

¹ The difficulty lies in the conclusion that on the ordinary wave theory calculations far too little energy would fall on a surface of the size of an atom (10^{-16} cm.²) even in one second to account for the energy of expulsion of the electron. Thus from a standard candle the energy incident per second on unit surface 3 metres away is about one erg (Drude, *Physical Optics*), so that under this light only 10^{-16} ergs would fall per second on an atom, and since about 10^{-12} ergs is required for the photo-electric effect occurring about the middle of the visible spectrum it should take several hours' illumination from the above source under the above conditions to make emission possible. Electron emission, however, is observed to take place immediately the substance is illuminated.

This difficulty is not resolved even by applying an important theoretical result obtained by Raleigh (*Phil. Mag.*, **32**, 188, 1916), namely, that an atom may absorb radiation from a region of area of the order of the square of the wave-length of the incident light rather than from an area of the order of the cross section of the atom itself. For visible light the distinction is very great, but vanishes for γ or X-rays, for example, where the wave-length is of the same order as the linear dimensions of the atom; yet in the latter case photo-electric emission commences immediately although it has been calculated on the classical wave-spreading theory that the γ ray energy from radium should require an immense delay before electron emission could take place.

frequency), the speed of the electrons increases as the frequency increases.

These two facts, although nearly incomprehensible on the ordinary wave theory, would accord with the old corpuscular theory were this not rendered wholly inadmissible on other grounds. An attempt to find an explanation of these facts by modifying the wave theory was made by Sir J. J. Thomson (*Proc. Camb. Phil. Soc.*, **14**, 421, 1908). The following account is in the main a quotation—

The [radiant] energy travelling outwards [from the radiating source] with the wave is not spread uniformly over the wave front, but is concentrated on those parts of the front where the pulses are travelling along the lines of force;¹ these parts correspond to the bright specks, the rest to the dark ground. . . . The energy of the wave is thus collected into isolated regions, these regions being the portions of the lines of force occupied by the pulses or wave motion. In fact, from this point of view, the distribution of energy is very like that contemplated on the old emission theory, according to which the energy was located on moving particles sparsely disseminated throughout space. The energy is, as it were, done up into bundles, and the energy in any particular bundle does not change as the bundle travels along the line of force. Thus, when light falls upon a metal plate, if we increase the distance of the source of light, we shall diminish the number of these different bundles or units falling on a given area of the metal, but we shall not diminish the energy in the individual units; thus any effect which can be produced by a unit by itself, will, when the source of light is removed to a greater distance, take place less frequently, it is true, but when it does take place it will be of the same character as when the intensity of the light was stronger. This is, I think, the explanation of the remarkable result discovered by Lenard, that though the number of corpuscles emitted by a piece of metal exposed to ultra-violet light increases [as intensity increases], the velocity with which individual corpuscles come from the metal does not depend upon the intensity of the light. If this result stood alone, we might suppose that it indicated that the forces which expel the corpuscles from the metal are not the electron forces in the light wave incident on the metal, but that the corpuscles are ejected by the explosion of some of the molecules of the metal which have been put into an unstable state by the incidence of the light, if this were the case the velocity of the corpuscle would be determined by the properties of the atom of the metal, and not by the intensity of the light, which merely acts as a trigger to start the explosion. Some experiments made quite recently by Dr. E. J. ~~Ladenburg~~ make, however, this last explanation exceedingly improbable. ~~Ladenburg~~ has investigated the velocities of corpuscles emitted under the action of ultra-violet light of different wave-lengths, and finds that the velocity varies continuously with the frequency, according to his

¹ Thomson assumes that the ether has disseminated through it discrete lines of electric force, these being in a state of tension. The light consists of transverse vibrations travelling along these lines.

interpretations of his experiments, the velocity is directly proportional to the frequency.¹ Thus, though the velocity of the corpuscles is independent of the intensity of the light, it varies in apparently quite a continuous way with the quality of the light; this would be very improbable if the corpuscles were expelled by an explosion of the molecule. It seems more reasonable to suppose that the velocity is imparted by the light, and yet, as we have seen, the velocity is independent of the intensity of the light. These results can, however, be reconciled by the view stated above, that a wave of light is not a continuous structure, but that its energy is concentrated in units (the places where the lines of force are disturbed), and that the energy in each of these units does not diminish as it travels along its line of force. Thus if a unit by impinging on a molecule can at any place make it liberate a corpuscle, it will do so and start the corpuscle with the same velocity, whatever may be the distance from the source when it strikes the molecule; thus the velocity of the corpuscles would be independent of the intensity of the light. Ladenburg found that the velocity of the corpuscle increases with the frequency of the light; this shows that, if the view we are discussing is correct, the energy in the units will increase with the frequency of the light. This latter statement is, of course, in general agreement with the quantum hypothesis, according to which the energy in any unit is directly proportional to the frequency.

To show by an extreme case how *few* light units it is necessary to postulate, say, in the visible region of the spectrum under ordinary conditions, Sir J. J. Thomson has carried out the following calculation. Light of such intensity that 10^{-4} ergs fall on unit area per second would be very faint, but would still be visible. If we think of a cylinder of ether, base 1 square centimetre and 3×10^{10} cms. in length, then the above-mentioned intensity is such that 10^{-4} ergs are distributed throughout this cylinder (at any moment), and the density of the light is therefore $\frac{10^{-4}}{3 \times 10^{10}}$ ergs per c.c. Taking as a mean value for one quantum the number 10^{-12} ergs, we see that there will only be *one* such unit in every 1000 c.c. of space. The structure of light is therefore of a coarse-grained character. A further point still remains to be mentioned. The idea of a point source not radiating uniformly (this being a result of the heterogeneous nature of emission) seems to be in disagreement with the ordinary laws of propagation of light equally in all directions. It must be remembered, however, that any physical source of radiation consists of a very large number of resonators, so that the total radiating effect is on the average symmetrical about the source.

It is necessary, however, to point out certain objections which can be urged against the ether string idea. These are given by Millikan (*The Electron*, p. 229) as follows:—

“Two very potent objections, however, may be urged against all

¹As already stated, the evidence now available shows that the square of the velocity of the electron is proportional to the frequency of the light.

forms of ether-string theory. The first is that no one has ever yet been able to show that such a theory can predict any one of the facts of interference. The second is that there is direct positive evidence against the view that the ether possesses a fibrous structure, as postulated by any form of ether-string theory; "each unit of positive electricity being the origin and each unit of negative electricity the termination of a Faraday tube"; then the force acting on one single electron between the plates of an air condenser cannot possibly vary *continuously* with the potential difference between the plates. Now in the oil drop experiments [*cf.* Vol. I., Chap. I.] we actually study the behaviour in such an electric field of one single isolated electron and we find, over the widest limits, exact proportionality between the field strength and the force acting on the electron as measured by the velocity with which the oil drop to which it is attached is dragged through the air. When we maintain the field constant and vary the charge on the drop, the granular structure of electricity is proved by the discontinuous changes in the velocity, but when we maintain the charge constant and vary the field the lack of discontinuous change in the velocity disproves the contention of a fibrous structure in the field, unless the assumption be made that there are an enormous number of ether strings ending in one electron. Such an assumption takes all the virtue out of an ether-string theory."

This criticism, however, scarcely bears on the view which at the present time (1924) appears to be gaining ground, *viz.* that discrete light quanta do actually exist, each quantum being capable of altering enormously in size.

Einstein's Equation for Photo-electric Emission.

On the basis of light assumed to exist actually in bundles or quanta, *i.e.* the discrete view of radiation, Einstein (*Ann. Physik* [iv], **17**, 132, 1905; *ibid.*, **20**, 199, 1906) deduced the following expression which connects directly Planck's constant h with the phenomenon of photo-electric emission—

$$Vc. = \frac{1}{2}mv^2 = h\nu - h\nu_0$$

where $\frac{1}{2}mv^2$ represents the maximum kinetic energy of the electron emitted by light of frequency ν . ν_0 is the threshold frequency already defined, characteristic of the substance from which the electrons are emitted. The significance of eV has already been pointed out. It follows from the above expression that when $\nu = \nu_0$ the electron will just be emitted without sensible speed, ν_0 being therefore the lower limit of frequency capable of bringing about the photo-electric effect at all. Further, the equation expresses the fact that the kinetic energy of the electron is proportional to the frequency, that is, the square of the velocity varies as the frequency.

This equation has been subjected to very rigorous test as will be indicated below. The remarkable conclusion is that the equation holds with the highest degree of accuracy in spite of the fact that the theoretical

foundation upon which it was based has now to be regarded as rather dubious. The equation is essentially an empirical one for which a basis has as yet to be found.

Regarding the kinetic energy term which appears in the Einstein equation above a remark has to be made concerning the significance of the term "maximum". The point has been emphasised by Richardson (*British Ass. Report*, 1921). "Owing to the fact that the emitted electrons may originate from different depths in the metal, and may undergo collisions at irregular intervals it is only the *maximum* kinetic energy of those which escape which we should expect to exhibit simple properties."

A further point concerns the significance of the threshold frequency ν_0 . Richardson (*loc. cit.*) states that if we measure the threshold frequencies for any pair of metals and at the same time measure the contact difference of potential V_0 between them then we find that V_0 is given by—

$$V_0 = \frac{h}{e}(\nu_0 - \nu'_0)$$

where ν_0 and ν'_0 are the threshold frequencies of the two metals. Further, we have seen earlier in this chapter that contact potential can be related to thermionic emission, being in fact the difference of two W terms, which are therefore related closely to the threshold frequency of the photo-electric effect. That so simple a relation holds is in itself somewhat surprising. Thus we would expect "the thermionic value to be an average taken over those electrons which get out. The photo-electric value, on the other hand, should be the minimum pertaining to those internal electrons which have most energy."

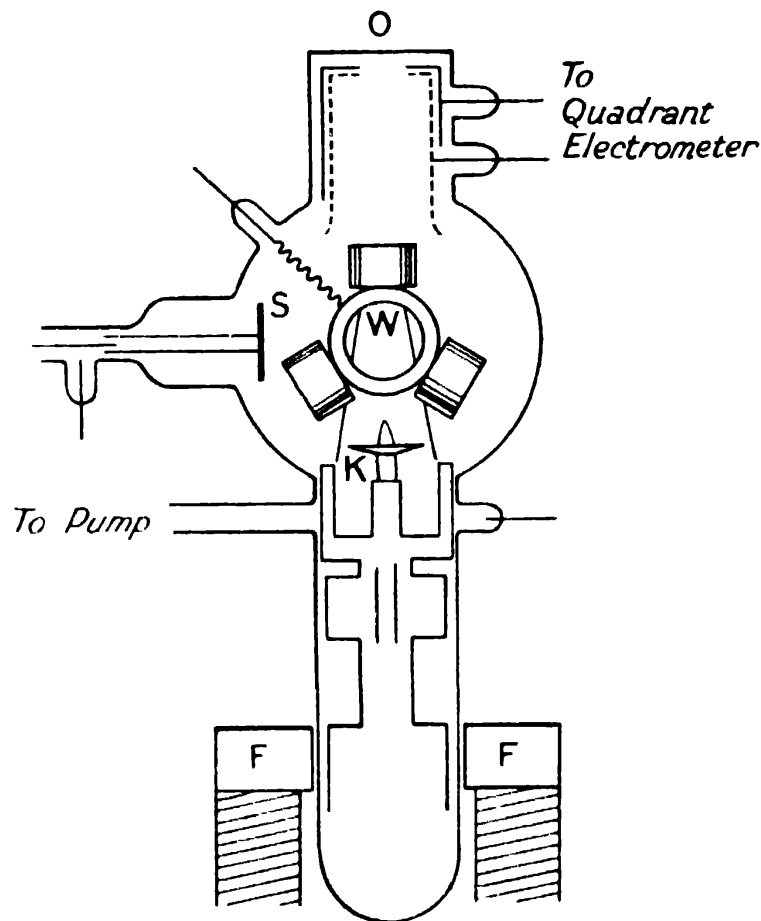
The question of the true basis of the Einstein photo-electric equation has engaged much attention but up to the present it has by no means been satisfactorily explained. It will suffice to mention here a recent attempt in this connection made by Whittaker on the basis of the Ewing magnetic model dealt with in the preceding chapter.

"Suppose that light of frequency ν is incident on a metal. There are grounds for supposing (*cf.* J. J. Thomson, *Phil. Mag.*, **37**, 434, 1919) that in a complex body such as a metal there are systems whose natural frequencies of vibration are distributed almost continuously over a wide range of frequencies. We shall therefore suppose that the incident light provokes resonance in a system within the metal, consisting of a magnetic wheel linked with a wire circuit [or rim] as described *loc. cit.*; so that the system absorbs energy from the incident light and the magnetic wheel is set in rotation. This absorption of energy from the incident light proceeds continuously. Suppose now that one of the free electrons happens to be in the vicinity of the magnetic wheel: the field due to the rotation of the wheel will cause the free electron to be sucked inwards to the wheel. If the energy of rotation of the magnetic wheel is less than the amount $U = h\nu$ the free electron, after, having been sucked in a certain distance, will be rejected without passing through the wheel or having (in the long run) abstracted any energy from it;

but if the energy which the magnetic wheel has absorbed from the incident light happens to be at the moment equal to or greater than $h\nu$, then the free electron will be sucked *through* the magnetic wheel and will come out on the other side, having abstracted energy of amount precisely $h\nu$ from the wheel. Thus when the energy absorbed by an atom of the metal from the incident light amounts to as much as $h\nu$ the first free electron which presents itself is sucked through the atom and relieves the atom of the energy $h\nu$. The electron, then, arrives at the inner surface of the metal on its way out with energy $h\nu$; it loses energy $h\nu_0$ in passing through the surface where $h\nu_0$ is equal to Richardson's product Φe in thermionics; and thus the energy with which an electron escapes from a metal illuminated by radiation of frequency ν is $h(\nu - \nu_0)$."

Millikan's Experimental Test of Einstein's Photo-electric Equation (cf. Millikan, Physical Rev., 7, 362, 1916)

Einstein's equation states that the kinetic energy of the escaping electron is a linear function of the frequency of the incident light. In



FIG

order to test this most rigorously it is necessary to employ a number of frequencies of monochromatic light covering as wide a range as possible. For this reason Millikan chose the alkali metals, since these respond

throughout practically the whole of the visible region as well as the ultra-violet. The choice of such material, however, greatly increases the experimental difficulties, since it is essential to work completely *in vacuo*. A diagrammatic sketch of the salient points of Millikan's apparatus is given in the accompanying Fig. 14.

Cast cylinders of the metals were placed on the wheel W which could be rotated by an external electromagnet so as to bring each metal in turn opposite the point O at which a beam of monochromatic light was incident. Clean metallic surfaces—an essential point—were obtained by cutting shavings from each metal *in vacuo* by means of the knife K. The energy of the electrons emitted under the influence of the light was estimated by applying to the metallic surface a positive potential just strong enough to prevent any of the discharged electrons from reaching the gauze cylinder opposite (shown by the dotted lines) and thus communicating a negative charge to the quadrant electrometer attached to the gauze. For a complete test of the Einstein equation it is necessary also to measure the electromotive force between the new surface and the test plate S. This was done by another electromagnetic device.

The results obtained showed that a very exact linear relation obtains between the frequency of the incident light and the applied positive voltage. Further, the slope of this curve should be h/e , and since e is known the photo-electric effect should thus be capable of yielding a value for h . Owing to the high degree of accuracy with which the Einstein equation holds a correspondingly accurate value of h can be obtained, the most reliable value, according to Millikan, from this kind of measurement being—

$$h = 6.56 \times 10^{-27} \text{ erg-sec.}$$

SELECTIVE PHOTO-ELECTRIC EFFECT.

Elster and Geitel in 1894 discovered that in certain cases the photo-electric effect depended upon the plane of polarisation of the incident light. The substance examined by them was the liquid alloy of sodium

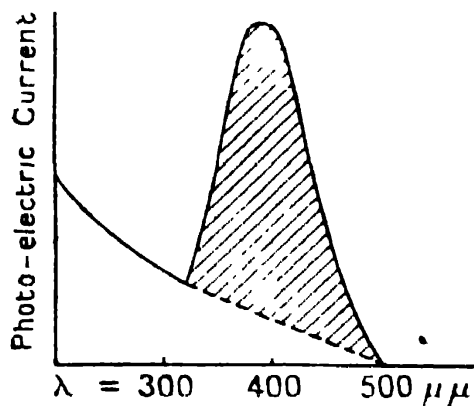


FIG. 15.—The dotted line indicates the normal effect; the maximum, the selective effect.

and potassium. It was found that when light fell upon the surface at an angle of 45° , a *maximum* photo-electric current was produced when the electric vector of the light was vibrating in the plane of incidence. (Compare, however, the conclusions arrived at by Millikan, *infra*.) Further, in this so-called selective effect the number of electrons emitted has a maximum value for a particular frequency of the light. This maximum value occurs at a wave-length somewhat shorter than the threshold wave-length λ_0 (for the normal effect).

and is not to be confused with λ_0 itself. For wave-lengths shorter than that corresponding to the maximum emission the selective effect rapidly falls off. The relative magnitude of the normal and selective effects are shown in the diagram (Fig. 15).

The position of the maximum in the selective effect occurs at the wave-lengths given in the following table (quoted from Hughes' *Photo-electricity*) :—

Substance.	Maximum Selective Effect Occurs at
Rb	470.510 $\mu\mu$
K	410
Na	340
Li	280
Ba	280

The same effect is observed when the metals are in the colloidal state in photo-electric cells. Thus the maximum sensitivity of such cells occurs at the following wave-lengths :—

Rb	480 $\mu\mu$
K	440
Na	320
Cs	550

No general agreement has yet been arrived at regarding the relation of the selective to the normal effect. As indicating the obscure nature of the selective effect, it may be mentioned that Wiedmann (*Ber. d. Deutsch. phys. Gesell.*, **18**, 333 (1916)) has found that the presence of hydrogen gas is essential to the production of the selective effect in the case of potassium. If the metal be repeatedly distilled *in vacuo* the selective effect is removed. It would be erroneous, however, to argue from this that the selective effect is accidental, due to some impurity. It is possible that in Wiedmann's case a temporary and unstable hydride is formed which, on decomposing, leaves the metal atom in a chemically activated state—differing as regards its electronic arrangement from the normal atom. Such chemical activation has been assumed in other connections. In the present connection all this is speculative, however. According to Millikan and Souder (*Proc. Nat. Acad. Sci.*, **2**, 19 (1916)) there is an "essential identity" between the selective and photo-electric effects, evidenced by the following facts: the energy of emission is in all cases given by $\frac{1}{2}mv^2 = h\nu - p$, where p is the work necessary to separate an electron from the surface of the metal; the amount of emission is not dependent on the angle of incidence or on the azimuth of polarisation, but solely on the coincidence of the impressed frequency with the natural frequency; as an active gas acts progressively on a fresh surface the normal effect merges gradually into the selective.

As already pointed out in Chap. III., in connection with the fourth method of determining the characteristic infra-red frequency of a metal, Lindemann has suggested the following expression for the frequency

ν_{violet} which corresponds to the position of the maximum of the selective photo-electric effect :—

$$\nu_{\text{violet}} = 2\pi \sqrt{m r^3}$$

where n is the valency of the atom to which the electron belongs, m the mass of an electron and r one half of the distance between two neighbouring atoms. It will be observed that r^3 is proportional to the atomic volume V of the metal. Hence the greater the atomic volume the smaller, *ceteris paribus*, the frequency. This is in agreement with the idea that a large atomic volume means that the electron is less firmly held and can therefore be set into movement by a quantum of relatively small magnitude, *i.e.* at a longer wave-length, than is the case with a substance of small atomic volume. The above expression can be put in a form which is convenient to use by first determining the value of the constant outside the square root by comparison with a single experimental determination. Thus Lindemann writes—

$$\nu_{\text{violet}} = 4.594 \times 10^{10} \sqrt{V}, \text{ or } \lambda_{\text{violet in } \mu\mu} = 65.3 \sqrt{\frac{V}{n}}.$$

The following table indicates the degree of applicability of the formula :—

	Atomic Volume.	Calculated λ	Obs. λ
Cs	70.6	550 $\mu\mu$	550 $\mu\mu$
Rb	56.3	490	480
K	45.0	438	440
Na	23.5	317	320-340
Li	11.9	225	280
Ba	36.7	280	280
Sr	34.5	271	
Ca	25.4	233	
Mg	14	172	

Haber (*Verh. d. Deutsch. physik. Gesell.*, **13**, 1117, 1911) has given a very simple and interesting relation between the " ν_{violet} " and the Einstein infra-red characteristic frequency of the atoms of the same substance, which we may denote by " $\nu_{\text{infra-red}}$ ". This relation is—

$$\frac{\nu_{\text{violet}}}{\nu_{\text{infra-red}}} = \sqrt{\frac{M}{m}}$$

where M is the mass of the atom and m the mass of an electron. Haber has shown that this agrees extremely well with observed values. Thus, using Lindemann's formula just referred to to calculate ν_{violet} , one can make use of the Haber relation to calculate $\nu_{\text{infra-red}}$ and compare it with the values given by Lindemann's *melting-point* formula (for calculating $\nu_{\text{infra-red}}$). The results are as follows :—

Substance.	$\nu_{\text{violet}} \times 10^{-15}$	$\nu_{\text{infra-red}} \times 10^{-12}$ Calculated by Haber.	$\nu_{\text{infra-red}} \times 10^{-12}$ Calculated by Linde- mann's Melting-point Formula.
Li . . .	1.27	11.26	10.78
Na . . .	0.947	4.62	4.38
K . . .	0.685	2.55	2.57
Rb . . .	0.612	1.55	1.56
Cs . . .	0.546	1.108	1.135
I . . .	0.906	1.87	1.85

It is well known that under the action of light, especially ultra-violet light and X-rays, gases conduct electricity, *i.e.* they become ionised by the expulsion of an electron from a molecule, the electron soon attaching itself to a neutral molecule to produce a negative ion comparable in mass with the positively charged residue formed in the first instance. This phenomenon is a further instance of the photo-electric effect—probably the analogue of the selective effect.

For further information regarding the photo-electric effect, the reader is referred to Allen's *Photo-electricity* or to Hughes' *Photo-electricity*.

CHAPTER VII.

(Physico-chemical change in homogeneous systems)—Ionisation and resonance potentials—Photochemical reactions: Einstein's law of the photochemical equivalent—Photochemical sensitisation Thermal reactions in homogeneous systems: Reaction velocity from the standpoint of the quantum theory.

It would be quite beyond the scope of this book to attempt any systematic account of the phenomena associated with the conduction of electricity through gases, the mechanism of ionisation by corpuscles or electrons, by β rays (electrons emitted from radioactive bodies) and α rays (positively charged particles also emitted by radioactive bodies), and the liberation of electrons from (or the ionisation of) gaseous molecules and atoms by the action of visible or ultra-violet light or by means of X-rays. A very brief description of some of these phenomena in so far as they were involved in the question of the determination of the electronic charge has already been given in Chap. I. of Vol. I. together with references to further information to the now classical works of Sir J. J. Thomson and Sir Ernest Rutherford. We are concerned here with a consideration of the magnitudes of ionisation and resonance potentials more particularly from the point of view of possible quantum relationships.

As a starting point we may recall the fact that the passage of electrons through a gas causes the emission of radiation. It is now known that one or other of two distinct processes may be involved. These are considered below. In general, however, no effect at all is produced until the electrons have attained a certain velocity, *i.e.* a certain minimal kinetic energy. In an electric discharge tube the velocity necessary to cause emission of light is attained by the electrons (the cathode ray stream) before they have travelled far, for they (the electrons) move with a positive acceleration towards the anode.

Ionisation and Resonance Potentials.

In dealing with collisions between electrons and molecules or atoms it is necessary to distinguish between two *kinds*, namely elastic collisions and inelastic collisions. In the first, the time of contact or encounter is very short compared with the second. No "chemical" effects are produced as a result of such collisions, the particles separating in the same chemical state and with the same momentum (though not of course with the same direction) as they possessed prior to the encounter. These are the kind of collisions postulated in kinetic molecular theory,

to account for the behaviour of gases for example. In the second kind of collision the time of encounter is longer, the total momentum after collision is less than it was before, and there is opportunity of transfer of energy between the two particles, which may result in observable chemical or physical change. This is consequently the more important kind of collision from the standpoint of atomic interaction, ionisation, and resonance, etc., and it is exclusively with inelastic collisions that we have now to deal. Tate and Foote (*Proc. Nat. Acad. Sci.*, **4**, 9 (1918)) point out that "no considerable transfer of energy from the light electron to the relatively heavy gas can take place except when the time of encounter between electron and atom *bears some simple relation* to the characteristic period of one of the vibrational degrees of freedom in the atom."

Keeping to inelastic collisions it is essential to point out that two different *types* of inelastic collision have been observed in connection with the bombardment of a molecule by a moving electron. One of these under the simplest conditions results in the emission of a radiation of a *single* frequency, *without ionisation of the gas*, whilst the other type of inelastic collision ionises the gas and causes it to emit a composite spectrum of radiations. The potential which must be applied to the freely-moving bombarding electron to give the first type of encounter may be termed a *resonance potential*, that giving the second type an *ionisation potential*.

The emission of radiation in general is due to the *return* of an electron to its normal position in the molecule or atom. When resonance occurs the electron does not leave the molecule, but is forced out to an outer position or orbit by the act of collision of the molecule with the freely moving cathode ray electron which then passes on with diminished energy. The molecule is now in an abnormal state and quickly reverts to the normal, with emission of the same amount of energy as was communicated to it in the first instance by the collision. Under the simplest conditions of resonance this energy is emitted as a single line of frequency ν_r , the energy emitted from a single molecule being in fact $h\nu_r$. If, on the other hand, the collision has been sufficiently violent to eject completely an electron from the molecule, a free electron is thereby produced, *i.e.* the gas is ionised and in process of time such free electrons will return to positively charged molecules with emission of light (a spectrum) thereby reforming uncharged molecules. The different lines constituting the emission spectrum are due to electrons arriving at different orbits or positions, as already described in Chap. V.

The quantum theory is most simply applied by considering the limiting conditions of these two phenomena of resonance and ionisation respectively. Let us take the resonance effect first. Denote by $1/2mv^2$ the *smallest* value of the kinetic energy which the bombarding electron must possess in order to bring about the effect at all. It follows that when this energy has been transferred by collision to the molecule the bombarding electron will have been practically brought to rest. Under these conditions we can equate the kinetic energy transferred at the

collision to the energy of the radiation subsequently emitted (in the return of the molecule to the normal state), *i.e.*—

$$1/2mv^2 = h\nu_r.$$

The kinetic energy of the bombarding electron may also be written in terms of the accelerating potential of the field which, by acting upon the electric charge, gives the kinetic energy to the electron. The relation is—

$$eV_r = 1/2m\tau^2$$

where e is the electronic charge and V_r is the potential called the resonance potential of the gas. V_r is the smallest potential which is required to give to an electron the kinetic energy $1/2m\tau^2$ which will just enable the electron to bring about the resonance effect in a molecule with which it collides. The resonance effect is therefore described in terms of the quantum theory by the relation—

$$1/2m\tau^2 = eV_r = h\nu_r.$$

This expression is obviously closely analogous to Einstein's photo-electric equation. The relation has been tested and verified by observing the wave-length or frequency of the single line emitted during resonance, and from this calculating the potential the value of which is then compared with that directly observed. The actual methods of measurement will be found in the papers referred to below in connection with individual gases. By way of illustrating the applicability of the above relation the case of mercury vapour may be considered. The resonance potential¹ of this vapour is found to be 4.8 volts in round numbers, and from this it is easily calculated that the corresponding radiation should be $254\mu\mu$ approximately. Experiment has shown that this is actually the wave-length of the *single* line emitted by mercury vapour when the vapour is traversed by electrons whose velocities correspond with a potential of 4.8 volts. Further, in this case, there is a sharp band in the *absorption* spectrum of non-luminous mercury vapour at the same position (McLennan and Edwards, *Phil. Mag.*, **30**, 695 (1915)).

In the above discussion of resonance we have dealt with the phenomenon on the basis of a single resonance potential. Experiment has shown, however, that there are two resonance potentials characteristic of certain vapours and gases and in the case of mercury there is evidence of a third. Numerical values will be considered later. Let us now pass to the phenomenon of ionisation.

In the case of ionisation potentials we are dealing in general with values which are distinctly greater than those characteristic of resonance, the greater values being necessary to cause actual ionisation of the gas. In this case also a quantum relation has been found to hold which is in all respects analogous to that which applies to resonance. The relation is—

$$1/2m\tau^2 = eV_i = h\nu_i,$$

¹ As is pointed out later more than one resonance potential is frequently observed.

where $1/2mv^2$ stands for the minimum kinetic energy which the bombarding electron must possess in order to just ionise the atoms of the gas, V_i is the corresponding potential which is just sufficient to give the necessary kinetic energy to the electron, and ν_i is the *greatest* frequency of the radiation emitted. As a result of such bombardment the selection of the greatest or "limiting" frequency for the purpose of applying the above quantum relation in this case is easily understood in view of the fact that an ionisation potential, being greater than a resonance one, the conditions under which ionisation can be observed naturally involve the concomitant appearance of any resonance effects (emission lines) of which the vapour may be capable and will likewise include those wave-lengths of emitted radiation which are due to the freed electron returning, not to the stable position in the molecule, but to some of the outer possible positions which are at least temporarily stable. The *limiting* frequency emitted denotes the return of a free electron to the position of maximum stability, *i.e.* to the innermost orbit. It will be evident at once that the processes here envisaged are simply those which we have already considered in connection with Bohr's theory of, say, the Lyman series of emission lines exhibited in the far ultra-violet by the hydrogen atom. It has been found, in fact, that, *in the case of the alkali metals the ionisation potential of the vapour corresponds with the highest or convergence frequency of a series, called the "principal series," whilst the lowest resonance potential corresponds with the first or lowest member (longest wave-length) of the same principal series.* In the case of metals other than the alkalis, the resonance potentials correspond with the lowest (longest wave-length) member of series which differ in "spacing" from the principal series and to which other names are given. The series referred to, however, converge to an upper frequency limit which is also the limit of the principal series and which therefore corresponds with the ionisation potential of the atoms of the vapour considered. Thus theoretically from a spectroscopic examination of the gas or vapour and a determination of the limits of certain series of emission lines it is possible to calculate by means of the two quantum expressions stated above, the resonance and ionisation potentials respectively. For details of emission spectra and the various series into which the lines have been analysed the reader is referred to Baly's *Spectroscopy* (in this series of Textbooks) or to N. R. Campbell's monograph on *Series Spectra*, or to Foote and Mohler's *Origin of Spectra* (American Chemical Society Monographs).

In many cases, *e.g.* mercury, the ionisation potential corresponds with a wave-length which is so short that it would be impossible to determine it experimentally except perhaps with a vacuum spectrograph and fluorite prism. In such cases the limiting wave-length can be obtained by observing the nature of the lines emitted when the gas or vapour is ionised and by making use of the appropriate expression for the series the upper limit of which should correspond with the ionisation potential.

The limiting frequency in the spectrum of a gas or vapour has been

determined by a direct experimental method which is not limited by considerations such as those referred to in connection with purely spectroscopic methods. The method referred to is that of Richardson and Bazzoni (*Phil. Mag.*, **34**, 285, 1917). The radiation emitted from the ionised gas is allowed to strike a metallic target, thereby causing in turn a photo-electric emission of electrons, whose velocities depend on the frequency of the incident light. By employing a magnetic field it is possible to calculate the velocity of the fastest electrons thus emitted, and hence by making use of the expression: $1/2mv^2 = h\nu$, it is possible to calculate the limiting or maximum frequency of the light which caused the photo-electric emission, this light having its origin in the ionisation of the gas in the first instance. In this way these authors have found that the limit of the helium spectrum occurs at 42 to 47 $\mu\mu$. The hydrogen spectrum extends down to a limit somewhere between 83 and 95 $\mu\mu$ (probably near 90 $\mu\mu$), whilst in the case of mercury vapour the limit lies between 100 and 120 $\mu\mu$. The last value is in good agreement with that obtained by other means, *i.e.* from the magnitude of the ionisation potential. In the case of hydrogen the shortest wave-length obtained by the above method corresponds with an ionisation potential of 13.5 volts, whilst the potential calculated by Bohr is 13 volts in round numbers.

In connection with the limiting frequency (which corresponds to ionisation) it is also to be noted that the value lies fairly close to the so-called dispersional frequency, that is, a characteristic frequency (usually occurring in the extreme ultra-violet) which enters into the expression for the refractive index of a gas, in which the index is expressed as a function of wave-length or frequency. From refractive index measurements, therefore, carried out in the available region one can calculate the dispersional constant and consequently the convergence frequency at least approximately. An indirect method of calculating the dispersional frequency in the case of a number of gases with a high degree of accuracy is given by Baly (*Phil. Mag.*, **27**, 632, 1914).

Hitherto we have dealt with ionisation as though there were but one ionisation potential. In certain cases more than one ionisation potential has been observed, and the phenomenon may well be a general one. Thus, in the case of mercury vapour, Goucher (*Phys. Rev.*, **8**, 561, 1916) has found two ionisation potentials, at 10.25 and 19 volts respectively, in addition to the resonance potential at 4.9 volts. McLennan (*Proc. Roy. Soc.*, **91 A**, 485, 1915) seems to have been the first to suggest that more than one type of ionisation is to be expected, depending upon the actual nature of the effect brought about by the bombarding electron upon the gas atom or molecule. The different ionisation potentials where they are known will be considered in connection with individual gases and vapours.

As illustrating the magnitude of the values of resonance and ionisation potentials and the extent to which they are in agreement with the values calculated on the spectroscopic basis, the data obtained by Tate and Foote (*Phil. Mag.*, **36**, 75, 1918) and by Foote, Rognley and

Mohler (*Phys. Rev.*, **13**, 68, 1919) for the vapours of the alkali metals are given in the following table:—

ALKALI METALS.

Metal (Vapour).	Resonance Potential.		Wave-length in Å°.	Ionisation Potential.		Wave-length in Å°.
	Calculated	Observed.		Calculated.	Observed	
	Volt.			Volt.		
Lithium . .	1.839	—	6707.85	5.363	—	2299.67
Sodium . .	{ 2.092 } { 2.094 }	2.12	{ 5895.94 } { 5889.97 }	5.112	5.13	2412.63
Potassium . .	{ 1.602 } { 1.609 }	1.55	{ 7699.01 } { 7664.94 }	4.318	4.1	2856.69
Rubidium . .	1.581	1.6	7800.29	4.155	4.1	2968.40
Caesium . .	1.447	1.48	8521.12	3.873	3.9	3184.28

In the case of other metals the values quoted are due to Foote, Rognley and Mohler (*loc. cit.*) and to Mohler, Foote and Meggers (*Bull. Bur. Standards*, **16**, 725, 1920).

Metal.	First Resonance Potential.	Second Resonance Potential.	Ionisation Potential
Arsenic . .	Mean resonance potential = 4.7 volt.		11.5 volt.
Zinc . .	4.18	5.65	9.3
Cadmium . .	3.95	5.35	9.0
Mercury . .	4.76	6.45	10.2
Magnesium . .	2.65	4.42	8.0
Calcium . .	1.00	2.85	6.01

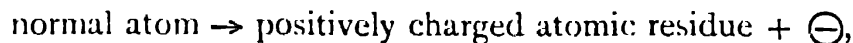
In all these cases there is satisfactory agreement between the observed resonance potentials and ionisation potentials and the values calculated from spectroscopic data. The behaviour of the metallic vapours may be briefly summarised as follows:—

Corresponding to the three types of collision we have three stages in the spectrum as the potential is increased. At the first resonance potential the corresponding line appears alone; above the second resonance potential two lines appear, and at the ionisation potential the entire arc spectrum appears. It is necessary to point out that in the case of such metallic vapours we are dealing with effects produced upon atoms as distinct from molecules.

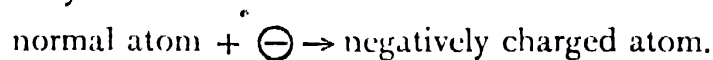
Symbolically the process produced by the impact of a free electron, having the energy corresponding with the resonance potential, may be represented as follows:—

normal atom → abnormal or activated atom.

Similarly, the ionisation process may be represented by—



where $\ominus$ is the conventional symbol for an electron. A process which is closely connected with that of ionisation, but is yet quite distinct, is represented by—



The energetics of this process, called the *affinity of a (neutral) atom for an electron*, will be considered in Chap. VIII. in connection with halogen atoms.

The behaviour of a number of gaseous elements in respect of resonance and ionisation will be considered in some detail later. As an illustration of the magnitudes obtained in the case of relatively complex organic molecules the following data due to Boucher (*Phys. Rev.*, **19**, 189, 1922) may be cited:—

Vapour.	Resonance Potential.	Ionisation Potential.
Benzene . . .	6.0 volts	9.6 $\pm$ 0.1 volts
Toluene . . .	6.2 $\pm$ 0.25	8.5 $\pm$ 0.5
Xylene . . .	6.5	10.0
Chloroform . .	6.5	11.5
Ether . . .	6.6 $\pm$ 0.1	13.6

The hydrocarbons have roughly the same ionisation potential, which in all cases is lower than that of hydrogen or oxygen (*q.v.*). It is not unlikely, however, that substances of this kind undergo decomposition at the same time and that therefore the values may not be completely characteristic of the substance originally introduced into the vessel.

The Rare Gases.

Helium.—The resonance potential of helium observed by Franck and Knipping (*Physikal. Zeitsch.*, **20**, 481, 1919) occurs at 20.5 volts, which is practically identical with the value 20.4 volts obtained by Horton and Miss Davies (*Proc. Roy. Soc.*, **95**, 408, 1919). Fricke and Lyman (*Phil. Mag.*, **41**, 814, 1921) have examined the emission spectrum of helium in the extreme ultra-violet and have located a fairly strong line at wave-length 585 Å, which would correspond to a potential of 21.2 volts, in satisfactory agreement with the resonance potential observed.

Franck and Knipping (*loc. cit.*)¹ have found an ionisation potential corresponding to the elimination of a single electron from the helium atom at 25.4 $\pm$ 0.25 volts, in excellent agreement with the value 25.0 obtained by Horton and Miss Davies (*Phil. Mag.*, **40**, 440, 1920). Cf. Bohr's atomic model for helium, Chap. V. The other less accurate

¹ More recent data, involving certain corrections, are given by Franck (*Zeitsch. Physik.*, **11**, 155, 1922).

methods of determination furnish results which are of the correct order of magnitude, e.g. the method of Richardson and Bazzoni. A second ionisation potential corresponding to the elimination of both electrons from the atom has been observed by Franck and Knipping at 79.5 ± 0.3 volts.

Neon.—The minimum resonance potential has been found by Horton and Miss Davies (*Proc. Roy. Soc.*, **98**, **A**, 124, 1920) in the case of this gas to occur at 11.8 volts, the minimum ionisation potential at 16.7 volts. A second resonance potential has also been found at 17.8 volts, and a second and third ionisation potential at 20.0 and 22.8 volts respectively. The existence of three ionisation potentials and two resonance potentials indicates that neon differs more from helium and argon than would have been anticipated. On the usual view the resonance and ionisation potentials correspond respectively with the lowest and highest frequencies of a certain series of emission lines. It would be expected therefore that there should be as many resonance potentials as there are ionisation potentials. The fact that only two resonance potentials apparently are found in this gas may be possibly due to two of them lying very close together, in which case one might escape detection. Another possibility is that the ionisation observed at one of three ionisation potentials is a spurious effect. The resonance potential 11.8 volts appears to be associated with the ionisation potential 16.7 volts, whilst the resonance potential at 17.8 volts seems to be associated with the ionisation potential 22.8 volts. If neon consists of two or more constituents having different resonance and ionisation potentials the critical potentials 11.8 and 16.7 would be ascribed to one isotope, the values 17.8 and 22.8 to the other.

Argon.—Horton and Miss Davies (*loc. cit.*) have also investigated this gas. Their final conclusions are that argon exhibits a resonance potential at 11.5 volts and an ionisation potential at 15.1 volts. The latter corresponds with the wave-length 817 Å. Lyman has found that the limiting wave-length of the argon spectrum lies very close to 800 Å. The agreement between the two results is satisfactory.

Diatomic Gases.

Hydrogen.—Owing to its simple structure and consequently its importance in connection with the various theories of atomic and molecular structure, hydrogen has been more frequently examined than any other substance. A brief review of the principal results obtained by various investigators will now be given. The following are those obtained by Franck, Knipping and Frl. Kruger (*Ber. Deutsch. physikal. Ges.*, **21**, 728, 1919).

First, there is a weak but appreciable ionisation of the gas at 11.5 ± 0.7 volts. This is ascribed to the ionisation of the molecule thus: $H_2 \rightarrow H_2^+ + \ominus$. In support of this view it is pointed out that the ion formed at this potential is of molecular and not atomic dimensions, thereby eliminating the possibility of ascribing the effect to

$H \rightarrow H^+ + \ominus$, which might be expected to occur at a higher potential. Sir J. J. Thomson has shown that the individual H_2^+ exists in the canal rays.

Secondly, a resonance potential is found at 13.6 ± 0.7 volts. This is ascribed to the dissociation of the molecule into its atoms followed by a further change in one of the atoms which now contains two quanta instead of the normal one quantum. The activated atom emits the first (lowest frequency) line of the Lyman series in the far ultra-violet. This potential is written by the authors as $(10.1 + Q)$ volts, where $Q = 3.53 \pm 0.25$ volts. This term is considered later.

Thirdly, a strong ionisation has been observed at 17.1 ± 0.27 volts, which is written as $(13.5 + Q)$ volts. This stage is regarded as the ionisation of the hydrogen molecule into an atom, a nucleus and a free electron, thus: $H_2 \rightarrow H + H^+ + \ominus$.

Finally, a new ionisation stage has been observed at the very high voltage 30.4 ± 0.5 , which is written by the authors as $(2 \times 13.5 + Q)$ volts, and corresponds with the most violent change of which the neutral molecule is capable, namely, ionisation into two nuclei and two free electrons, thus: $H_2 \rightarrow 2H^+ + 2\ominus$.

The quantity, Q , namely 3.53 volts, which apparently occurs in at least three of the observed stages, is ascribed to the dissociation of the hydrogen molecule into neutral atoms. As evidence of the general correctness of this view it is pointed out that 3.53 volts would correspond with 81,300 calories per gram-molecule of hydrogen, a quantity which agrees well with the heat of dissociation of the gas, 85,000 calories as determined by Langmuir. A resonance potential at the low value 3.53 was not actually observed. Its importance would suggest the carrying out of the necessary examination. It is of interest in this connection to note that Mohler and Foote obtained evidence of a slight resonance collision between 2.5 and 3.5 volts, but the value has not yet been accurately fixed. It may perhaps be pointed out that by subtracting stage 3 from the final stage referred to above we obtain the value 13.3 volts as the ionisation potential of the hydrogen *atom*, *i.e.* the true ionisation potential of atomic hydrogen. Bohr's theory of the hydrogen *atom* gives the ionisation potential as 13.54 volts, in very good agreement with the value obtained indirectly from the above investigation. It is noteworthy, that these authors did not observe, directly, an ionisation potential in the neighbourhood of 13.3 volts.

Values differing from those quoted above have been obtained by other workers. Thus Franck and Hertz, Bishop, Davis and Goucher, found somewhat earlier that ionisation sets in at a potential of about 11 volts, and the latter authors further found a second ionisation potential at 15.8 volts which does not find any confirmation in the work of Franck, Knipping and Frl. Kruger but is confirmed by the value 15.9 volts obtained by Compton and Olmstead (*Phys. Rev.*, **17**, 45, 1921). Hydrogen has also been investigated by Horton and Miss Davies (*Proc. Roy. Soc.*, **97**, A, 23, 1920) with the following results:—

First, there is a resonance potential at 10.5 volts. This is presumably

the same as that observed by Franck, Knipping and Fil. Kruger at 10.1 volts as a possible resonance potential of the hydrogen molecule. Horton, however, ascribes this effect as due to the atom by displacement of an electron from one orbit to another.

Secondly, a further resonance potential manifests itself at 13.9 volts. Horton ascribes this to radiation from the molecule. This is presumably the same as the resonance potential observed by Franck and his co-workers at 13.6 volts which they also ascribe to the molecule.

Thirdly, ionisation is found at 14.4 volts. This value does not appear to correspond with any found by other workers. It is rather striking, however, that 14.4 volts corresponds with the wave-length 84μ which lies very close to the accepted value of the dispersional wave-length for hydrogen, namely, 86 to 87μ . Horton ascribes this stage to the ionisation of the atom thus: $H \rightarrow H^+ + \ominus$. This value is much farther away from the value calculated by Bohr, namely, 13.54 volts, than is the value obtained by Franck.

Boucher (*Phys. Rev.*, **19**, 189, 1922) finds a resonance potential at 10.1 ± 0.1 volts and two ionisation potentials, namely at 13.6 and 15.6 volts.

Finally, Mohler and Foote (*Bull. Bur. Standards*, **16**, 669, 1920) have found a first resonance potential at 10.4 ± 0.5 volts, a second resonance at 12.2 volts approx. ; a first ionisation potential at 13.3 ± 0.5 volts and a second at 16.51 ± 0.5 volts.

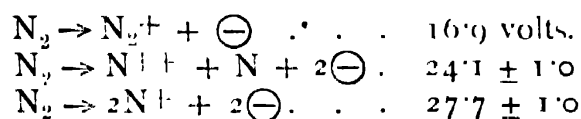
On the whole the various values observed, with certain exceptions, are in good agreement with those calculated from Bohr's theory especially as regards the atom. The Bohr theory leads to the following results:—

Resonance for the atom at 10.16 volts ; ionisation of the atom at 13.54 volts, ionisation of the molecule at 16.26 volts. The difference between the ionisation potential of the molecule (16.26) and the ionisation of the atom (13.54), namely, 3.24 ± 0.5 volts, should represent the energy of dissociation of the molecule into neutral normal atoms. This quantity is in fair agreement with the known heat of dissociation, as already pointed out.

Nitrogen.—The early experiments of Franck and Hertz led to the value 7.5 volts as the ionisation potential of this gas. In view of the known chemical stability of the molecule this value was surprisingly low. Davis and Goucher (*Phys. Rev.*, **13**, 1, 1919) showed later that this potential did not give rise to ionisation but to resonance. They found a more intense type of resonance at 9 volts and a true ionisation at about 18 volts. H. D. Smyth (*Phys. Rev.*, **14**, 409, 1919) found a marked resonance effect at 8.29 ± 0.04 volts, and evidence of ionisation at about 18 volts. Smyth comes to the very important conclusion that the resonance potential at 8.29 volts corresponds to the dissociation of the nitrogen molecule into neutral atoms. The effective wave-length is therefore 145μ , and the energy of activation 190,000 cal. per mole, a quantity which is about the order one would expect for the heat of dissociation. Boucher (*Phys. Rev.*, **19**, 189, 1922) finds the resonance potential at 8.4 ± 0.1 volts and an ionisation potential at 15.8 volts. Mohler and

Foote (*loc. cit.*) confirm the general accuracy of previous determinations of the resonance potential by finding the value 8.18 ± 0.10 volts. These authors find ionisation at 16.9 ± 0.5 volts, which is probably a fairly accurate value.

More recently, Smyth (*Nature*, **111**, 810, 1923) has found three critical potentials for nitrogen and has likewise determined whether the individual concerned is of atomic or of molecular mass. Smyth interprets his results as follows.—



Oxygen.—An early accepted value for the ionisation potential of this gas was 9 volts. Mohler and Foote (*loc. cit.*) have, however, carried out a careful revision and find a resonance potential at 7.91 ± 0.1 volts which would correspond with a wave-length of $155\mu\mu$ lying, therefore, in the broad and somewhat indefinite region in the extreme ultra-violet in which oxygen gas is known to exhibit marked absorption. Boucher (*loc. cit.*) obtained practically the same resonance potential, namely, 8.0 volts and also an ionisation at 14.0 volts, whilst Mohler and Foote had found ionisation at 15.5 ± 0.5 volts. It is noteworthy that the dispersional wave-length, namely, $83.8\mu\mu$ is equivalent to 14.3 volts, which would therefore seem to confirm Boucher's value.

Iodine Vapour.—Mohler and Foote (*loc. cit.*) find the resonance potential at 2.34 ± 0.2 volts, and the ionisation potential at 10.1 ± 0.5 volts. Compton and Smyth (*Science*, **51**, 571, 1920) find two types of ionisation, namely, a very weak ionisation at 8.5 volts which they attribute to the ionisation of the free iodine *atoms* formed in sensible amount by contact of the vapour with the hot filament in the experimental tube, and also a very intense ionisation at 10 volts attributed to the molecules. The difference, namely, 1.5 volts, should correspond with the net energy involved in the dissociation of a molecule of iodine into neutral atoms. This value, when converted into cal. per gram-molecule, namely, 35,000, agrees very closely, as it should do, with the known heat of dissociation. These authors have also examined this vapour in connection with the allied phenomenon of fluorescence. It is pointed out that the fluorescence is not usually accompanied by ionisation, and is therefore due to the shift of an electron from a position of high to one of low potential energy. The evidence in favour of this view in the case of iodine is as follows. The neutral molecule, as found by Compton and Smyth, requires 10 volts to bring about ionisation; the fluorescing molecule requires but 7.5 volts when excited by the green mercury line. The difference 2.5 volts corresponds with the quantum of energy of the mercury line as calculated by the relation $eV = h\nu$. This result is direct experimental evidence for the existence of molecules with abnormal energy content.

In general, in the case of diatomic gases, two distinct kinds of *molecular* ionisation may be anticipated. In the first the molecule parts

with an electron, but preserves its general molecular structure. This is the kind of molecular ionisation met with in the gases referred to above. "It seems probable that materials capable of ionising in this manner should possess a characteristic spectrum," Mohler and Foote (*J. Wash. Acad. Sci.*, **10**, 435, 1920). In the second kind of molecular ionisation, the molecule breaks up directly into a positive ion and a negative ion. This is the kind of ionisation encountered in the case of gaseous hydrochloric acid which will be discussed in connection with the energetics of the crystal lattice (Chap. VIII). "Materials which are ionised in this manner probably do not possess characteristic spectra in the ordinary sense," except that they exhibit the single line in the far ultra-violet corresponding with the act of union of the two ions. It may be expected that the alkali halides in the state of vapour would exhibit the latter kind of ionisation. This would explain the known absence of any emission spectrum characteristic of the salt. We would expect instead to observe the spectrum of the alkali metal produced by the recombination of the alkali ion with electrons. Further, it is known that the flame emission spectrum of the metals is suppressed by an excess of halogen. This finds a simple explanation on the basis that the excess of halogen in the flame ultimately gives rise to halogen ions in relatively large amount with which the metallic ions combine rather than with the electrons.

PHOTOCHEMICAL REACTIONS. EINSTEIN'S LAW CHEMICAL EQUIVALENT

PHOTO-

The most important application of the quantum theory to photochemical processes (*i.e.* processes in which high temperature radiation proceeding in a given direction from an external source acts upon a material system which is itself at a relatively low temperature) is that due to Einstein and known as *the law of the photochemical equivalent*.

According to this law a photochemical reaction takes place owing to the absorption of radiation, each single molecule of the photosensitive substance requiring just one quantum $h\nu$ (of the requisite frequency which the substance itself can absorb) in order that the molecule may be decomposed or otherwise changed.

This law was first enunciated by Einstein in 1912 (*Ann. Physik* [4], **37**, 832, 1912). The mode of deduction adopted by Einstein involved, however, a consideration of a mass action equilibrium between the photo-sensitive substance and its products of decomposition, the equilibrium position being altered by exposure to the external radiation. As has been pointed out by Ornstein and Burger (*Kon. Akad. Wetenschap. Amsterdam*, 1920) a true mass action equilibrium can only be realised when the temperature of the radiation and the matter is one and the same. Under photochemical conditions, as we have already seen (*cf.* Vol. II., chapter on Photochemistry) a photo-stationary state, as distinct from a mass action equilibrium, is set up. It is evident therefore that Einstein's original deduction of the law of the photochemical

equivalent is not as satisfactory theoretically as one could wish. Instead therefore of following Einstein's original method we shall follow that adopted later by him (*cf.* Einstein, *Physikal. Zeitsch.*, **18**, 121, 1917) an outline of which (in so far as it concerned Planck's radiation law) has already been given in Chapter V., in connection with Bohr's theory, in the section entitled: "Einstein's use of a generalised Bohr model to deduce the radiation law of Planck".

It will be assumed that the reader is familiar with the mode of treatment and the significance of the symbols employed in the section referred to. A simple and apparently sound deduction of the law of the photochemical equivalent is then obtained in the following manner.

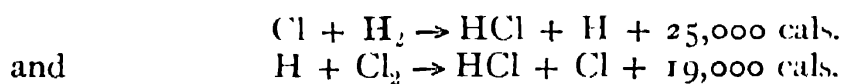
Consider the case of a gas at so low a temperature that in the temperature radiation (in equilibrium with the matter) the frequency ν corresponding to the changes $Z_m \rightleftharpoons Z_n$ is almost entirely negligible, *i.e.* there is practically no *thermal* chemical reaction at the temperature considered. Accordingly in the *unilluminated* gas, the state Z_m is very rare compared with Z_n , and we shall assume that in general almost all the molecules of the gas are in the state Z_n . Such molecules as happen to be in the state Z_m are assumed to be capable of undergoing a chemical elementary change (in place of, or rather in addition to, the change $Z_m \rightarrow Z_n$) analogous to a unimolecular reaction. It is further assumed that the velocity of this chemical change is great compared with the velocity of the change $Z_m \rightarrow Z_n$.

What will happen when the gas is illuminated with radiation of frequency ν ? The molecules will change steadily from state Z_n to Z_m by absorption of radiant energy $(E_m - E_n) = h\nu$, as we have already seen. These molecules will only to a very small extent, however, pass back into the state Z_n by spontaneous change or by "negative absorption". By far the greater number will carry out the chemical decomposition, since we have assumed a large reaction velocity for this process. Practically then $h\nu$ of radiant energy is absorbed per molecule decomposing, which is the law of the photochemical equivalent.

The identity of the above conclusion (for chemical change produced by radiation) with the expressions for the photo-electric effect, and for ionisation and resonance of gases and vapours, is obvious. It serves to show that these apparently diverse phenomenon have this fundamental quantum relation in common.

Passing to the experimental evidence in connection with Einstein's law of the photochemical equivalent we find a few cases, *e.g.* the photochemical decomposition of HBr and of HI gases, the photochemical decomposition of ozone in presence of helium, in which the law is obeyed. In many other cases, however, the law is apparently quite inapplicable, the amount of chemical change being either considerably greater or considerably less than would be anticipated on the basis of the energy absorbed if the law held good. Thus Henri and Wurmser (*Journ. Physique* [5], **3**, 305, 1913) found in the case of the photo-decomposition of hydrogen peroxide and of acetone in aqueous solution that the amount of energy apparently required was considerably less than that

demanded by Einstein's law; in fact, only 1 to 0.1 per cent. of the theoretical value. Henri and Wurmser believe that the light acts as a catalytic agency in such cases, accelerating but not initiating the reaction. Such a view is, however, not very helpful. Another case may be cited, namely, the photochemical union of hydrogen and chlorine gases, in which Bodenstein (*Zeitsch. Elektrochem.*, **19**, 836, 1913) has shown that the amount of hydrochloric acid produced is far in excess of what would be anticipated from the light absorbed provided the law held. The reason for this is almost certainly that advocated by Nernst (*Zeitsch. Elektrochem.*, **24**, 335, 1918), namely that the true photochemical process is the decomposition of a chlorine molecule into its atoms, this primary process being followed by two secondary processes, namely—



as well as the process, $\text{H} + \text{Cl} \rightarrow \text{HCl}$.

It is evident that on this basis a very small number of free chlorine atoms produced photochemically will ultimately give rise to a very much larger number of hydrochloric acid molecules. This number though large will not be infinite, however, because the free chlorine and hydrogen atoms will disappear gradually to yield chlorine molecules, hydrogen molecules, and also hydrochloric acid molecules in terms of the third process mentioned above.

The present position (1923) appears to be that Einstein's law of the photochemical equivalent is really exact, but that, (1), in the majority of cases the true photochemical process is masked by other concomitant processes which occur independently of the external radiation to which the system is exposed under typical photochemical conditions, (2) that an incorrect estimate of the actual amount of radiant energy converted into chemical change may be made owing to the possibility of an absorption and a degradation into longer wave (heat) radiation, with consequent rise in temperature of the system as a whole. The first set of conditions would mean that the amount of chemical change is much greater than that anticipated on the basis of the law; the second that the observed amount of chemical change would be much less than that anticipated. Further, Einstein assumes that the photochemical change is brought about by effectively monochromatic radiation of a definite frequency. As is well known, however, absorption bands exhibit width, especially when the concentration or density of the substance is high, and experiment goes to show that any wave-length inside a band is capable of bringing about the photochemical effect. It is hardly to be expected, however, that all wave-lengths inside a band will be equally efficient. To test the Einstein law in the most unequivocal manner it would be necessary to choose the wave-length which includes the head of the band exhibited by the substance.

It is apparent therefore that a satisfactory test of the validity of the law is not easy to realise. The use of the term photochemical has perhaps over-emphasised the necessity of experimenting in what may be

called the ordinary photochemical sense, although these were the conditions which Einstein had in mind. The principle ought to hold equally well for purely thermal conditions, *i.e.* conditions in which the temperature of the matter and of the radiation interpenetrating it are the same. The latter conditions indeed appear to be better adapted for testing the law not only on experimental grounds but also on theoretical.

An examination of the applicability of the law to so-called thermal changes, *i.e.* photochemical changes, in which the radiation and matter are at the same temperature, is given in the concluding section of this chapter.

A critical survey of the experimental photochemical work which has been carried out in connection with the law of the photochemical equivalent is given in Appendix VII.

Photochemical Sensitisation.

Photochemical or optical sensitisation has already been discussed briefly in Volume II. Chapter on Photochemistry. Two of the best known instances are (1) the sensitisation of the photographic plate by the addition of a dye which itself absorbs the light to which it is intended that the plate should be made sensitive, and (2) the photo-sensitisation of certain gaseous reactions on addition of chlorine (*cf.* Weigert, *Ann. Physik*, **24**, 243, 1907). Recently the same idea has been applied by Baly and his co-workers (*Journ. Chem. Soc.*, 1921 *passim*) to the part played by chlorophyll, the green colouring matter of the plant leaf, in bringing about the union of CO_2 and H_2O to form formaldehyde, which in its freshly synthesised form polymerises to sugars. Apart from the sensitiser, chlorophyll, the union of CO_2 and H_2O could only be brought about by radiation of the extreme ultra-violet region, since it is only in this region that these substances exhibit absorption. In the presence of chlorophyll, however, the union can be brought about by light of the visible spectrum, and it is undoubtedly such light that is utilised by the plant itself.

A simpler case of apparently similar sensitisation has been discovered by Franck (*Zeitsch. Physik*, **9**, 259; **11**, 161, 1922), namely the dissociation of molecular hydrogen into the atomic form by collision of H_2 molecules with mercury atoms which are themselves activated by being exposed to radiation of $\lambda = 2536.7 \text{ \AA.}$, emitted from a quartz mercury lamp. It is believed, on the basis of the thermal dissociation of hydrogen as viewed in the light of the radiation hypothesis of *thermal* chemical change (*cf.* concluding sections of this chapter) that radiation of wave-length $3200 \text{ \AA.}$ (and possibly shorter wave-lengths) should be capable of decomposing molecular hydrogen into neutral atoms. Hydrogen gas, however, is apparently quite transparent for all wave-lengths in the visible and ultra-violet up to the excessively short wave-length $1200 \text{ \AA.}$ Consequently no *direct* photochemical decomposition of hydrogen by radiation in the nearer ultra-violet, say $3200 - 2000 \text{ \AA.}$,

is to be expected. But mercury vapour is known to possess an absorption band with its head at 2536 Å., and consequently, Franck argued that, if this vapour be activated by exposure to radiation of this wavelength region, the activated mercury atoms by collision with intermixed hydrogen molecules might discharge their excess energy into the hydrogen molecules at the moment of collision and so bring about dissociation of the hydrogen. Possibly a collision is a favourable circumstance for such transfer, although it is not quite clear whether the energy transferred is actually in the form of radiation or not. (Franck himself does not regard the transfer of energy as taking place via radiation.) By the use of an oxide (reducible by atomic but not by molecular hydrogen) present in the experimental vessel it was shown that dissociation of the hydrogen molecules actually takes place. It is evident that this type of photochemical induction may find wide application in bringing about photochemical change, which cannot be brought about by direct exposure to radiation as ordinarily employed. If at the collision the transfer is actually radiational, localised so as to be equivalent to an extremely high radiation density, then the results obtained serve to indicate that the absence or apparent absence of a band due to its extreme narrowness is not an infallible guide to the non-decomposability of a molecule. On this point, however, we know almost nothing.

THERMAL REACTIONS IN HOMOGENEOUS SYSTEMS. REACTION VELOCITY FROM THE STANDPOINT OF THE QUANTUM THEORY.

By the term thermal reactions is meant reactions of the "ordinary" kind which proceed without being exposed to any definite external source of short-wave radiation such as we meet with in the so-called photochemical reactions. The fundamental difference between the two kinds of reaction is the fact that in photochemical reactions, as ordinarily carried out, the temperature of the active radiation is very much higher than the temperature of the material system affected, whilst in the case of thermal reactions, the temperature of the radiation is so far as this is effective is identical with that of the material system itself.

Photochemical phenomena have demonstrated the fact that chemical change can be brought about as a result of absorption of radiation in the short-wave region. We are led to generalise this and to seek in radiation of longer wave-length the ultimate cause of ordinary or thermal reactions as well. It is obvious that every material system, in virtue of its temperature, contains radiation at the same temperature as that of the matter itself. Under ordinary conditions, *i.e.* at ordinary temperatures, this radiation is mainly of the infra-red type. Theoretically, wave-lengths belonging to all regions of the spectrum are present, but it is only the infra-red region which contributes a sensible amount of energy. It is well known that electro-magnetic properties of substances, *e.g.* the dielectric constant, are intimately connected with the radiation density in the material, and further, such properties have a marked effect upon the chemical reactivity of molecules, *e.g.* the electrolytic dissociating power of solvents which possess high dielectric constants. This

suggests, therefore, that infra-red radiation is at least one of the sources of the energy which is required to bring about ordinary or thermal reactions.

The suggestion, that the existence of photochemical change (using the term in its ordinary sense as referring to effects produced by *short* wave radiation) may be used as an argument for attributing *all* chemical change to radiation, seems to be due, in the first place, to Trautz (*Zeitsch. f. wiss. Photogr.*, **4**, 1906). Trautz's suggestion remained, however, relatively unfruitful, due no doubt to the fact that at that time the quantum theory had not begun to attract much attention, and Trautz himself did not apply it till later (Trautz, *Zeitsch. anorg. Chem.*, **102**, 81, 1918).

In 1911 E. Kruger advanced the view that infra-red radiation was the cause of such phenomena as solution pressure, dissociating power of a solvent, electrolytic dissociation and solubility of a solute. This is dealt with in Chapter IX. Kruger did not, however, consider the question of chemical kinetics or the influence of temperature and of catalysts upon velocity constants.

The first definite argument pointing to the necessity of regarding radiation as playing an essential part in chemical change is due to Perrin (1913) (*cf. Les Atomes*, translated into English by D. L. Hamnicks, 1916). Perrin there takes up the crucial case of the *uni*-molecular process. The argument is given below in Perrin's own words. (It should be noted that Perrin uses the term light to denote radiation in general.)

... "the rate of dissociation at constant temperature, in unit volume of a gas A, for a reaction of the following kind:—



is proportional to the concentration of the gas A and cannot be altered by the addition of other gases to the reacting system.

"In other words, for a given mass of the substance A, the proportion transformed per second is independent of the dilution; if the given mass occupies ten times more space, its concentration then being ten times less, then ten times less will be transformed per litre, or just as much in all as before dilution. Thus, contrary to what one might have expected, the number of impacts has no influence on the rate of dissociation. Out of the given N molecules of the gas A, always the same number will decompose per second (at a given temperature) whether the gas is relatively concentrated or mixed with other gases (in which case impacts will be frequent) or whether it is dilute (when impacts will be rare). . . . Molecules do not decompose by striking against each other and we may say: *The probability that any molecule will be ruptured does not depend upon the number of impacts it receives.*

"Since, however, the rate of dissociation depends largely upon the temperature, we are reminded that temperature exerts its influence by radiation as well as through molecular impact, and we are faced with the suggestion that the cause of dissociation lies in the visible and invisible light that fills, under stationary conditions, the isothermal

enclosure wherein the molecule of the gases under consideration are moving.

"*The essential mechanism of all chemical reaction is therefore to be sought in the action of light upon atoms.*"

[Lindemann, on the other hand (*Trans. Faraday Soc.*, Part III., Vol. 17, 1922), has pointed out that the observed unimolecular process might be accounted for by supposing that "a molecule after acquiring by collision the increment of energy necessary for decomposition, did not necessarily decompose at once, but that on the average a certain time elapsed before an activated molecule decomposed, during which it might be de-activated by a further collision. If the number of molecules entering and leaving the active state per second is large compared with the number undergoing chemical change,¹ then the supply of active molecules is maintained constant though the total concentration be varied over a wide range. At some sufficiently small concentration, however, the frequency of collision between molecules would become too small to maintain the supply of active molecules, and a falling off in the velocity constant would result."]

To render the radiation hypothesis applicable it is necessary to express it in terms of the quantum theory. This was done independently by Perrin in a paper, the publication of which was delayed until 1919 (*Ann. de Physique*, p. 1-108, 1919), and also by W. C. McC. Lewis (*Trans. Chem. Soc.*, 1914 onwards). The methods of treatment have much in common but are by no means identical. The main idea common to both is that Einstein's law of the photochemical equivalent (according to which one quantum of absorbable radiation causes one molecule to decompose or react) is applicable to thermal reactions as well as to photochemical. The present position of the radiation hypothesis will be gathered from a discussion on "Catalysis with Special Reference to Newer Theories of Chemical Action," *Trans. Faraday Soc.*, 17, Part III., 1922.

In the outline given below it will be observed that we are concerned, in the first place, with a statistical result (independent of quantum mechanics) referring to the internal energy of molecules, and then with the conditions of reactivity on the radiation hypothesis.

The Concept of Critical Increment or Energy of Activation.

For our present purpose the most significant phenomenon associated with thermal changes is the influence of temperature upon the reaction velocity, the velocity constant increasing three or four fold for a rise of 10° in the neighbourhood of room temperature. An effect so great as this cannot be accounted for simply on the basis of an increase in the *average* kinetic energy of translation of the molecules, for in the

¹ It will be observed that the assumption made here regarding the relative speed of chemical change and of reversion to the normal reactant state respectively is precisely the opposite of that made above in deducing the law of the photochemical equivalent.

most favourable case this increase would not account for more than 2 per cent. of the observed effect, and it might be argued that the kinetic energy effect would not even be in the right direction. We shall assume, however, for the sake of argument, that the change in kinetic energy would be in the right direction.

On the basis of Maxwellian distribution of velocities we know that whilst the average increase in kinetic energy for, say, a ten degrees rise in temperature is negligibly small, there must be a small fraction of the molecules with an exceedingly great kinetic energy, which fraction will increase with temperature relatively rapidly, and it might be argued that these molecules with exceptionally great kinetic energy of translation are the chemically active ones. Perrin has shown, however, that the average life of a molecule is quite independent of kinetic energy considerations and consequently even the fastest moving molecules are not more likely to be chemically active than the slow ones. In view of Perrin's conclusion, however, we may be justified in eliminating kinetic energy of translation from our considerations. This is true without qualification for unimolecular processes. For bimolecular processes (in which the kinetic energy of translation which leads to collisions makes union or reaction between two molecules possible at all although it does not determine whether a collision shall be *chemically* effective) the rate of reaction at a given temperature does depend upon the *average* speed of a molecule, *i.e.* upon the average collision frequency, but as already pointed out, even in the most favourable case, the increase in chemical rate due to this factor is only about two per cent. of the observed effect produced by the rise in temperature. Hence even in bimolecular processes considerations of collision frequency are only of minor importance in respect of the total influence exerted by alteration in temperature. This is further borne out by the experimental fact that the observed influence of temperature upon reaction velocity is much the same for a unimolecular process as it is for a bimolecular process, being in fact somewhat *greater* for the unimolecular.

To account for the influence of temperature upon chemical velocity constant, therefore, *from considerations based upon the molecules themselves*,¹ since we have seen that kinetic energy of translation is inapplicable, we are forced to conclude that the effect is due to alteration in the *internal* energy of the molecule; in other words, that it is the internal energy which determines whether a molecule is chemically reactive or not. (In the case of bimolecular processes the question of orientation at a collision might likewise be a determining factor; nothing is known at present (1923) about this aspect of the problem, beyond the fact that, in the case of the bimolecular decomposition and reformation of gaseous hydrogen iodide, orientation considerations seem to be unnecessary, since the observed chemical speed can be accounted for without having

¹ Considerations based upon the molecules themselves, *i.e.* upon their state or properties, may be justified by the results to which they lead, but they are obviously incomplete in that they do not offer an explanation of the existence of the postulated physical or chemical state or attributes.

recourse to them (*cf.* Lewis, *Trans. Chem. Soc.*, **113**, 471, 1918). It might be argued, however, that in this case the molecules which react are of so simple a structure that orientation would not enter sensibly here.)

At first sight the substitution of internal energy considerations in place of kinetic energy considerations appears to have little advantage. From measurements of specific heat it is known that, *on the average*, the increase in internal energy per degree rise in temperature is not large. In the simplest case the increase in internal energy varies directly as the absolute temperature, and hence a rise of ten degrees would cause an increase of approximately 3 per cent. in the average internal energy at ordinary temperatures. The observed influence of temperature upon the velocity of chemical change cannot be ascribed, therefore, to the *average* increase in internal energy. When heat is added to a body, however, the energy does not distribute itself evenly among the molecules; instead, some receive no energy, others a moderate amount, and a very few receive excessively great amounts of energy. It would seem, therefore, that chemical reactivity itself as well as the influence of temperature on reaction velocity is to be sought in the fact that a very small number of molecules contain at any moment an abnormally large quantity of internal energy. As the temperature is raised the *proportion* of such molecules increases rapidly and such molecules can be regarded as the chemically reactive ones. (The term "reactive" as used here is to be distinguished from the term "active" used later in connection with physical isomers.)

From this point of view the rate of a unimolecular process is directly proportional to the number of reactive molecules per unit volume, the proportionality factor in this case being quite independent of temperature. In the case of *unimolecular* change it is difficult, as a matter of fact, to say whether molecules in the reactive state possess a real existence as distinct from the resultant molecules. We are here thinking of a simple unimolecular dissociation involving the separation of two of the constituent portions of a molecule. If the act of separation is catastrophic we could deny the existence of the active form, since this would only represent a momentary phase through which the molecular system passed on its way in the act of decomposing. No physical distinction would appear to be possible between reactive resultants and reactive reactant.

If the reactive state, in a unimolecular change, be regarded as *incapable* of independent existence, it would follow that the rate at which the molecules become reactive (*i.e.* the number whose internal energy content attains a certain limit per second) is *identical* with the observed rate of chemical change. If, on the other hand, the reactive state is regarded as being capable of independent existence, this would imply that the rate at which the molecules become reactive is greater than (and may be much greater than) the rate at which the reactive form undergoes chemical change into resultants. It would imply further that the condition which determines the number of molecules attaining a

certain internal energy content per second is not in itself sufficient to determine the rate of the chemical process, since some other condition is required to determine the probability of decomposition of the reactive forms. It must be confessed that at present (1923) no general agreement has been reached on the question.* The assumption that the rate at which the reactive state is attained is identical with the chemical rate observed is the simpler of the two possibilities, but that of course is not decisive.

In the case of bimolecular processes there seems little doubt but that reactive molecules have a real independent existence, the observed rate of reaction being directly proportional to the frequency of collision between the reactive individuals. The proportionality factor in this case is, however, not wholly independent of temperature, since it measures the probability of collision and this in turn varies as the square root of the absolute temperature. It is to be observed that this statement, regarding the part played by collision frequency and consequently by the kinetic energy of translation, does not contradict the conclusion arrived at above to the effect that a collision *per se* does not endow a molecule with chemical reactivity. The temperature determines the number of reactive molecules in existence (in a bimolecular process) as well as the frequency of collision; only a very small fraction of the total collisions is chemically effective. We have now to consider how the above conceptions can be expressed in a quantitative form.

By treating the problem of reaction velocity from the point of view of statistical mechanics as applied to internal energy it is possible to correlate the velocity constant with the temperature, as has been done by Marcelin (1913) (*cf. Ann. de Physique*, **3**, 120, 1915), and later in a more exact manner by J. Rice (*Brit. Ass. Rep.*, 1915, p. 397). The relation between the observed velocity constant k and the absolute temperature T for a simple type of gaseous reaction is shown by Rice to be—

$$d \log k/dT = (E + kT)/RT^2$$

or approximately $d \log k/dT = E/RT^2$.

In deducing this expression it has been assumed that a molecule reacts, *i.e.* decomposes immediately (reactive state as distinct from resultant is non-existent), when its internal energy has been raised to a certain critical value which is in general large compared with the average internal energy of the molecule. This critical limit is known as the critical energy of the molecule. The term E denotes the difference between the critical energy and the average or mean internal energy reckoned per gram-molecule. E may therefore be called the critical increment or energy of activation; E denotes the amount of energy which has to be added to make an average [gram]-molecule react. It is at this point that the radiation hypothesis of chemical reactivity enters, the assumption being that the quantity E is contributed by the absorption of infra-red radiation of a given frequency which the substance is capable of absorbing. It is assumed that the communication

of this energy is governed by quantum mechanics as applied to radiation. A different view of the mechanism of energy-transfer will therefore be taken according as we assume the validity of Planck's first, second, or third formulation of the theory (*cf.* Chap. II.).

If the reaction, whether unimolecular or polymolecular, be reversible, it follows, on the statistical basis of the expression, that the reactive resultants have exactly the same critical energy as the reactive reactants. This does not mean that the E term is the same for both reactant and resultant.

Granted that the critical increment is due to radiation, and further assuming that a single quantum is capable of accounting for the E of a single molecule, it can be easily shown from a knowledge of the magnitude of the temperature coefficient of a reaction, that the effective radiation must belong to the short infra-red region, *i.e.* of the order 1 to 3μ , in the case of reactions which occur with sensible velocity at ordinary temperatures.

It will be observed that the Marcellin-Rice equation is identical in form with the equation $d \log k/dT = A/RT^2$, where A is a constant having the dimensions of energy, an equation first proposed by Arrhenius in 1889 (*Zeitsch. physikal. Chem.*, **4**, 226), and which is known to be in good agreement with experiment. (The applicability of the equation of Arrhenius has already been discussed in Vol. I.). The treatment underlying the Marcellin-Rice equation attributes a certain physical meaning to the term A , provided A and E are identified. A somewhat different meaning was attributed to the A term by Arrhenius himself, which raises a consideration of great importance.

Perceiving the close analogy in form between the equation of van't Hoff, namely, $d \log K/dT = Q_v/RT^2$ (where K is an *equilibrium* constant and Q_v is the nett heat absorbed at constant volume in a chemical process obeying the law of mass action), and the equation $d \log k/dT = A/RT^2$, where k is a *velocity* constant, Arrhenius was led to regard the A term as essentially similar in meaning to the Q_v term, *i.e.* A was regarded as the nett heat absorbed when one mole of "inactive" molecules became transformed into one mole of "active" molecules, these being the terms first used by Arrhenius. In this sense A is called a heat of activation. If this is correct, it implies that the active and inactive forms of one and the same chemical substance are to be regarded as "thermodynamically distinct" substances. In other words, the active and inactive forms are physical isomers, *i.e.* the distinction between them although real cannot be expressed, as in the case of chemical isomers, by attributing a different grouping and attachment of atoms in a molecule. Physical isomers cannot be represented by different structural formulæ such as are employed to differentiate chemical isomers.

We are dealing with a more subtle distinction, dependent not on different points of attachment but on a different spatial configuration, in the sense that one physical isomer would be a more "distended" form than another physical isomer. It is in this sense, and in this sense only, that we speak of them as having different structures. Naturally

such distension involves alterations in the intensity and direction of the inter-atomic forces. This aspect of the difference is considered in more detail later in connection with the force field theory of chemical reactivity.

The change from one physical isomer to the other, assuming for simplicity that there are but two composing the whole of the substance examined, is brought about, as suggested by Arrhenius, as a consequence of energy absorption or evolution. The important question arises as to whether the distinction between and existence of the physical isomers is solely one of energy or whether physical structure in the sense alluded to above is to be considered as well. In other words, are the concepts of energy content and physical structure to be regarded as distinct from one another, or is structure simply the dependent concomitant of a given energy content? If the latter view is correct then the *existence* of a limited number of physical isomers, say two, would mean an almost inconceivable mode of distribution of internal energy, in that such energy would have to be regarded as distributed in two and only two ways in respect of amount, for of course if the internal energy were distributed (as one would in general expect) in a very large number of unequal amounts this would mean—on the basis that energy content as such sufficed to distinguish one isomer from another—that a correspondingly large number of physical isomers were capable of existence, a view which is fatal to the concept of distinct physical isomers limited in number. It would seem necessary, therefore, to make a *real* distinction between physical structure and energy content. (Incidentally it would be somewhat easier to contemplate this distinction in terms of an essentially static atomic structure such as that of Lewis and Langmuir than it would be on the basis of a dynamic one such as that of Bohr.)

The same conclusion is arrived at if we return to the meaning attributed by Arrhenius to the *A* term, namely the heat of activation of the inactive form. As thus employed the *A* term is completely analogous to the nett heat term which governs the variation with temperature of the equilibrium constant of a chemical reaction in the ordinary sense. In the latter case the heat of reaction at constant volume is defined thermodynamically as the difference between the *average* internal energy contents of the reactants and resultants. The use of the term average implies that there is a statistical distribution of internal energy content amongst the molecules of the reactant as well as of the resultant, in which a very few molecules possess an abnormally high or an abnormally low energy content. If we transfer this idea to the case of the conversion of an inactive physical isomer into a so-called active one—as we are bound to do if the *A* term is really analogous to a Q_p term—it would necessarily follow that the molecules comprising, say, the inactive form are similar to one another in physical structure but possess very different energy contents, the *average* of which is low, whilst the molecules comprising the active form are also similar to one another in respect of structure (which differs from that of the inactive form), but again have a statistical distribution of energy, the *average* value of which is

high. In so far, therefore, as we can come to any definite conclusion in the matter at all it would seem necessary to believe—provided physical isomers, limited in number, exist at all—that these are thermodynamically distinct in respect of physical structure, but that such distinction does not necessarily imply that a given individual molecule of one isomer at a given moment of time shall have a different energy content from an individual molecule of the other isomer. * This conclusion, as will be readily seen, indicates that the term active has been employed by different investigators in a somewhat ambiguous sense. It seems generally agreed that before a molecule can become chemically reactive its energy content must have attained a certain value. If this is so, then *all* the molecules of the so-called active isomer are not chemically reactive, since, if the preceding argument is correct, an active molecule has not necessarily attained the required energy content, although the majority of the active molecules will be reactive because their *average* internal energy has, by definition, attained the necessary magnitude.

In the above we have been considering the question of active and inactive states in terms of the postulated existence of a limited number of distinct physical isomers. For the sake of making the contrast clear, let us revert to the wholly different concepts underlying the Marcellin-Rice equation, which tacitly assumes that a given substance is a thermodynamically single entity. This equation is based on classical statistical mechanics which means that all values of internal energy-content are taken as possible, *i.e.* the gradations of energy-content are continuous. This is equivalent to saying that there is a semi-infinite number of physical isomers (if energy content were taken to define an isomer completely) and to say this is equivalent to discarding altogether the concept of *such* isomers as thermodynamically distinct forms. The point as to whether it is justifiable to treat a fraction of the molecules of a homogeneous unary substance as thermodynamically distinct from the remainder is referred to by Tolman (*Journ. Amer. Chem. Soc.*, **42**, 2506, 1920). It would certainly seem to be quite unjustifiable. The Marcellin-Rice considerations, in fact, give no information one way or the other as to whether one or more distinct physical isomers exist in a given system. If a few, say two, isomers do exist, and if one of these is called active with respect to some chemical change which the substance can undergo, then the Marcellin-Rice equation is to be taken as applying not to the observed velocity constant of the process but to *the rate at which the inactive form changes into the active*. The E term which appears in the Marcellin-Rice equation is the critical increment of the inactive form, *i.e.* the energy which must be added per mole of inactive form (in the average state as regards internal energy) in order to transform it into an average mole of the active form. This would mean that numerically the E term is identical with the A term in spite of the fact that the velocity constants which appear in the equation of Marcellin and of Arrhenius are different, the first referring to the rate of activation of the inactive form, the second to the rate of the subsequent chemical reaction. Although A and E may thus have the same numerical value it

is to be remembered, however, that they represent different concepts, for the *A* term, which is identified with a *Q* term, is therefore given in general by the difference between two opposing *E* terms, one of which, however, in the case envisaged appears to be zero. The relation of *E* to a heat effect is discussed in Chap. IX. It need scarcely be emphasised that the *A* term, although identified with a heat effect, must not be identified with the true nett heat effect of the subsequent chemical process. The nett heat effect of the latter is in fact the difference of the *E* terms of reactant and resultant, and, consequently, numerically the nett heat effect of the observed process is the difference of two opposed *A* terms.

The Arrhenius treatment implies, as already mentioned, that the active form (in respect of its average internal energy content) requires no further addition of energy to enable it to take part in the chemical change. The number and kind of physical isomers characteristic of a given substance determine to a large extent the number and kind of reactions in which the substance can take part. If the substance happens to exist in only one physical state, then the concept of physical isomer does not enter and the substance as a whole has to be treated directly in terms of the Marcellin-Rice equation.

In considering the Marcellin-Rice equation attention has already been called to the difficulty presented by the unimolecular process, namely, as to whether the molecules which have received the necessary amount of energy have a finite life or not. Precisely the same difficulty presents itself when the matter is viewed from the standpoint of actual distinct physical isomers. As already mentioned, the problem is not as yet solved. It is somewhat significant perhaps that the cases to which the concept of physical isomers has been applied, have involved ultimately poly-molecular reactions. In such cases there is no particular difficulty in envisaging the real existence of active molecules whether these are characterised only by having high energy content, or characterised by high internal energy content and special physical structure.

Viewed from the standpoint of mechanics it is evident that the Marcellin-Rice treatment is more fundamental in character than is that based solely on the existence of physical isomers. The attempt to combine both ideas is made above, because possibly it gives a more *general* picture than either concept alone can afford. Thus assuming that, say, two physical isomers actually exist, one of which is termed active the other inactive, it is evident that the problem of accounting for the influence of temperature upon an *observed* velocity constant involves the effect of temperature upon the equilibrium constant between the active and inactive forms, and this in turn could be analysed into two opposing velocity constants at least one of which (namely that governing the change from the inactive to the active form) is affected by temperature in terms of the Marcellin-Rice equation. The active form, or to speak more precisely, the major portion of the active form, is, as already pointed out, chemically reactive in respect of the subsequent observed chemical change.

The treatment of the problem of the effect of temperature upon an observed velocity constant, as outlined above, on the basis of the real existence of physical isomers may be put in a quantitative form as follows :—

Neglecting for the moment the difficulty already alluded to in connection with unimolecular processes, we shall choose such a process for the sake of simplicity of treatment, *i.e.*, we are assuming for the moment that the active form has a real existence even in the case of unimolecular change. The two forms, active and inactive, are assumed to be in mass action equilibrium with one another, this equilibrium being attained practically instantaneously. Denoting the equilibrium constant by K , we have

$$K = [\text{actives}] / [\text{inactives}]$$

whence,

$$d \log K / dT = Q_0 / RT^2$$

where Q_0 is the heat absorbed in transforming one gram-molecule of the inactive into the active form. Q_0 is to be distinguished from the observed heat of the subsequent reaction, which is in fact the difference of two opposing Q_0 terms. We shall assume further, with Arrhenius, that the concentration of actives is small compared with that of the inactives. Then—

$$\begin{aligned} \text{observed rate of the unimolecular process} &= k_{\text{obs.}} \times [\text{total reactant}] \\ \text{or observed rate} &= k_{\text{obs.}} \times [\text{inactives}], \end{aligned}$$

where $k_{\text{obs.}}$ is the observed unimolecular velocity constant.

Regarding the same process from the point of view of the active form of the reactant we can write—

Observed rate of the unimolecular process = $k_0 \times [\text{actives}]$, where k_0 may be regarded as the *true* unimolecular constant of the reaction. It follows from the above relations that,

$$\begin{aligned} k_0 &= k_{\text{obs.}} [\text{inactives}] / [\text{actives}] \\ &= k_{\text{obs.}} / K. \end{aligned}$$

On taking logarithms and differentiating with respect to temperature we obtain—

$$d \log k_0 / dT = d \log k_{\text{obs.}} / dT - d \log K / dT.$$

Writing $d \log k_{\text{obs.}} / dT = A / RT^2$ (equation of Arrhenius), and $d \log K / dT = Q_0 / RT^2$,

we obtain—

$$d \log k_0 / dT = A / RT^2 - Q_0 / RT^2.$$

Since k_0 refers to the velocity in terms of actives it follows that k_0 itself will not vary with temperature, so that the term on the left-hand side of the above equation is zero, and consequently we obtain the Arrhenius result—

$$A = Q_0.$$

Naturally if the active form (in the Arrhenius sense) can revert to the inactive form, without first receiving an increment of energy, it would follow that the E term of Marcelin and Rice becomes numerically identical with A or Q_0 , although the physical meaning of E has to be distinguished from the physical meaning of A .

It may be remarked that since we are regarding a very limited number of physical isomers as possessing real existence, it would follow that in certain cases or under special conditions the material examined might conceivably exist in one form only, usually the so-called inactive form, or more probably whilst existing in two forms the change over from inactive to active might be slow. Such behaviour may be the cause of the remarkable physical properties found by Baker (*J. Chem. Soc.*, **121**, 568, 1922) for certain liquids. It may be recalled that Arrhenius himself regarded a substance as consisting mainly of the inactive form but that the change over into the active form was rapid.

In view of the somewhat tentative nature of the conclusion to which we have come as regards distinct physical isomers, it is of importance to take into account other evidence which bears upon the question of the existence of isomers as distinct entities. This is afforded by the work of E. C. C. Baly on the basis of spectroscopic observations.

The Force-Field Theory of Chemical Reactivity.

(*Cf.* Baly, *Journ. Amer. Chem. Soc.*, **37**, 979, 1915 (a summarising paper); also *Phil. Mag.*, **40**, 15, 1920. In both papers references to other publications are given. *Cf.* also Stark, "Atomdynamik".)

It has long been believed that there exists a definite correlation between the primary chemical structure of the molecule and the type of light absorption which it exerts. This has been maintained notably by Hantzsch who when he succeeded in preparing five differently coloured alkali metal salts from one colourless acid attributed essentially different structural formulæ to them all (Hantzsch, *Ber.*, **42**, 966, 1909; *ibid.*, **43**, 45, 1910). Later, however, the same investigator obtained a number of different modifications of *m*-nitroaniline and was forced to confess that there was not enough different formulæ denoting *chemical* isomers to go round (*Ber.*, **43**, 1662, 1910).

Baly's interpretation of the spectroscopic results obtained by him and other investigators leads to the conclusion that a given type of absorption neither indicates nor is accounted for by a given structural formula. Instead, the character of the absorption is taken to indicate a state of chemical reactivity in which the substance is at the moment existing. The argument together with a few applications thereof, expressed in Baly's own words, is as follows:—

"It follows from the Zeeman effect, that is to say, the resolution of spectrum lines into doublets, triplets, etc., in a powerful magnetic field, that the particles or atoms producing these lines must possess [electro]-magnetic fields of their own. . . . While these atomic fields have been taken into consideration in explaining such physical phenomena as the

above, their influence upon the properties of molecules does not seem to have received notice. These fields must possess both a polar and a quantity factor, and it would follow that atoms which are markedly different in their chemical properties must differ markedly in the polar factor of their force fields. When two such atoms approach one another sufficiently closely the force lines due to their respective force fields will tend to condense together with the loss of energy and with the formation of a condensed field. . . . On these lines, therefore, it may be said that the chemical reaction or combination between the two atoms is due in the first instance to the force fields appertaining to the two atoms.

"Turning now to the compound that is produced, it is evident that the general stability will depend upon the condensed force field between the atoms.

"If a molecule of one compound reacts with a molecule of another compound such reaction takes place in virtue of their respective force fields. If these fields are of opposite type the force lines of the two will condense together, with the result that an addition compound of the two is formed. . . . If, owing to the inherent properties of the atomic fields, the force lines can form a completely closed system, then the molecule will possess no reactivity. If two such molecules with completely closed fields are brought together it is evident that they can have no influence upon one another, and, further, this absence of influence will be entirely independent of what their chemical properties in solution would lead us to expect. It would seem that in this fact is to be found the explanation of the absence of any reaction between HCl and NH_3 , 2H_2 and O_2 , 2CO and O_2 , etc., in the complete absence of water. . . . An exactly similar explanation holds good for the converse case, namely that NH_4Cl , when dry, does not dissociate into HCl and NH_3

"On the other hand, although a certain amount of condensing together of the force lines due to the atomic fields must occur, *ex hypothesi*, yet by no means must the resulting force fields always be entirely closed. When the maximum possible condensing together of the force lines has occurred with the maximum possible escape of energy, there may be left over an uncompensated balance of force lines. This residuum will determine the properties of the given molecules, and will give rise to what has long been recognised by chemists as residual affinity. . . . Among chemical compounds which possess a balance of uncompensated force lines or residual affinity water may be mentioned as a very typical example. . . .

"From what has been said already, it is obvious that if the closed force field of a molecule be opened or unlocked its reactivity will be enhanced. This unlocking may be brought about in two ways, namely, by the use of a substance possessing residual affinity, or by the action of light. The simplest case to consider is that of the solution of the closed-force-field molecules in a solvent possessing residual affinity. . . . Clearly, however, the case is an absolutely general one."

In addition to the opening up of the closed fields by means of a

solvent we have also to consider the opening up produced by absorption of light.

"The light in being absorbed does work upon the closed fields and opens them, and this gives a rational explanation of the selective absorption of light. An example of the opening up of the closed molecular force field by means of light is found in the union of hydrogen and chlorine. When in the dark and at ordinary temperatures, the force fields of these gasses are closed and they have no action upon one another. Under the influence of ultra-violet light the reaction to form HCl proceeds owing to the opening up of the closed fields by the light and the amount of combination is a function of the amount of light energy absorbed. . . .

"When a substance is dissolved in a solvent it is clear that there must be set up generally an equilibrium condition. . . .

"If the case be considered of a complex molecule, it is clear that the force field of that molecule will be complex. . . . It would be expected that the influence of a solvent upon a complex force field would be progressive and that it would attack various portions of the field in turn. It indeed follows that the opening up of a complex field must take place in definite stages, the number of stages depending upon the complexity of the field. Each of these stages will be influenced by light so that each stage must be characterised by its power of absorbing definite light rays and may be differentiated in this way because the light waves absorbed by the various stages will be different. Very typical examples of compounds which are opened up in stages are the β -substituted naphthalene compounds, which as a rule in alcoholic solution show three absorption bands. Three stages in the opening up of the force fields must, therefore, coexist in the solvent, each one characterised by its power of absorbing definite rays of light. In concentrated sulphuric acid solution the absorption spectrum is very different, since other stages are called into play, but usually one of these stages at least is common to the two solvents. . . . Each opened stage must possess a definite reactive power towards other molecules." Certain experimental evidence may now be presented.

Baly and Marsden (*J. Chem. Soc.*, **93**, 2108, 1908) "investigated the absorption spectra of certain aromatic amino-aldehydes and ketones and found that the alcoholic solutions of these compounds exhibit a well-marked absorption band. The addition of a small quantity of alcoholic HCl to any one of these solutions causes the development of a yellow or red colour which disappears when more of the acid is added. The colour is due to the appearance of a new absorption band nearer to the red than that shown by the parent compound. On addition of the excess of acid the absorption spectrum changes to that of the hydrochloride of the amino base, which somewhat resembles that of the free base itself. It is clear from these results that the conversion of the amino bases to their hydrochlorides is not simply an addition reaction. There is no doubt that it is not the amino compound such as exists in alcoholic solution which forms the salt, but that the first quantity of the

acid converts the base into an intermediate form and it is this intermediate form which reacts with more acid to give the salt. . . . The addition of the first quantity of HCl opens the closed fields to a higher stage which is evidenced by the characteristic light absorptive power, and the field must be opened to this stage before the molecule can react to give the salt. These results also have a bearing on the application of the theory to catalysis. When the above amino compounds are treated with methyl iodide they tend to give their methyl derivatives. The velocity of this reaction is known to be materially increased when some acid is added. The acid has been shown to open up the closed systems to a higher stage with a greater reactivity and therefore it acts as a positive catalyst in the methylation of these compounds."

"Exactly analogous results have been obtained by Baly and F. O. Rice (*J. Chem. Soc.*, **101**, 1475, 1912) in the sulphonation of aromatic phenol ethers. In this case it was found possible to convert the whole of the reacting substance into the intermediate form and to observe its change into the sulphonic acid. . . . In the sulphonation reaction, when the compounds are dissolved in cold concentrated sulphuric acid, they are in many cases entirely converted into the intermediate stage which frequently is characterised by its absorption of visible light, so that the solution is visibly coloured. On standing, the system is slowly changed to the sulphonic acid and the progress of the reaction can be followed by the spectroscope. The absorption spectrum of the sulphonic acid differs entirely from that of the intermediate stage, and somewhat resembles that of the original substance in alcoholic solution. It is perhaps worth mentioning that if the sulphuric acid solution, before the sulphonation has taken place, is poured on to ice, the original compound is recovered in a pure state. These two investigations establish beyond any doubt the existence of the intermediate stage in a chemical reaction, such as was deduced from the force-field theory.

"The fact that the existence of the various stages in the opening up can be recognised by their characteristic light absorption enables us to interpret absorption observations with considerable certainty. . . . Rice and Baly (*J. Chem. Soc.*, **103**, 2085, 1913) have found that the nitro derivatives of benzene tend to exist with their force fields very definitely closed. This results from the difference between the affinities of the phenyl nucleus and the nitro group. Such a compound would naturally tend to be affected differently by a strong acid and by a strong base. The absorption of nitrobenzene in solution in dimethyl aniline and in concentrated sulphuric acid is entirely different; indeed, the former solution is coloured red whilst the latter is colourless. Clearly, therefore, the manner of opening up the force fields is different, according to whether an acid or basic solvent is used, and so we may speak of nitrobenzene as being amphoteric."

It may be pointed out that on Baly's theory, in so far as it is concerned with the interpretation of absorption bands, it is concluded that of two bands exhibited by a given substance, that one which lies towards the red end of the spectrum indicates a higher stage of activation than

is indicated by the band lying in the violet direction. On the basis of the quantum theory the band towards the red corresponds to a smaller quantum than does the band towards the violet. The active form requires a smaller amount of energy to attain some (unspecified) standard state than is required by the inactive form, which requires a larger quantum and consequently absorbs in the violet in order to attain the standard state.

“In the case of inorganic acids, base and salts, ionic dissociation is the extreme case in the opening up of their force fields. . . .

“It is in organic chemistry that the force-field theory finds its most obvious application, for so few of the reactions are ionic.”

It has already been mentioned that the absorption bands exhibited in the visible and ultra-violet are interpreted on the above theory as indicating different physical isomers or “molecular phases”. Baly has further endeavoured to show that these bands are integral multiples of a fundamental infra-red band, and on this basis has developed relationships between bands in various parts of the spectrum in terms of energy quanta characteristic of the particular atomic and molecular systems considered. This method of treatment has already been briefly referred to in connection with the infra-red absorption spectra of gases (Chap. IV.).

That a nascent molecule or molecule at the moment of its formation is in an abnormal or active state has been fairly generally suspected. The views outlined above tend to give some degree of precision to this idea. It is on this basis that Baly, Heilbron, and Barker (*Journ. Chem. Soc.*, 1025, 1921), for example, explain the abnormal reactivity of formaldehyde (when synthesised photochemically) as is evidenced by its capacity to polymerise to sugars. A similar enhancement has been observed by T. B. Johnson and Bass (*Journ. Amer. Chem. Soc.*, **44**, 1341, 1922) in the case of nitrile produced *in situ* by the decomposition of imido-esters. Under these conditions the nitrile tends to polymerise to cyclic derivatives, although no such polymerisation of ordinary nitrile takes place. Undoubtedly numerous other examples of this kind exist.

The concept of physical isomers likewise plays a fundamental part in Smit's theory of allotropy (*cf.* Smit's book translated by J. S. Thomas in this Series of Textbooks).

On reviewing the matters dealt with in the two preceding sections there appears to be a reasonable amount of experimental justification for the actual existence of distinct physical isomers, each possessing a statistical distribution of internal energy amongst the molecules pertaining to any one form, the average energy content of one physical isomer differing from that of the other by the amount $A \equiv Q_0$, either of which terms becomes numerically equal to the E term of the inactive form (provided the active form is capable of reverting to the inactive form without any preliminary absorption of energy). The observed rate of the chemical change cannot be greater than the rate at which the inactive form changes into the active.

Conditions for Reactivity on the Radiation Hypothesis.

In connection with the Marcelin-Rice equation it was pointed out that the energy represented by the critical increment E might be regarded as obtained from the thermal radiation present in the system in virtue of its temperature, this statement constituting, in fact, the radiation hypothesis of chemical reactivity. To express this idea quantitatively recourse must be had to the quantum theory.

In order that any of Planck's relations may be applied it is essential that temperature radiation alone be considered, that is, that the radiation and the matter composing the system be in temperature equilibrium. On Planck's view, the interchange between matter and radiation is effected through the medium of oscillators, situated on the molecules of the substances composing the system. In the case of thermal reactions occurring at constant temperature in a thermostat (which defines the temperature of the system both with regard to the radiation and to the material), Planck's theory may be applied with some degree of certainty. In this connection the following statement made by Planck (*Theory of Heat Radiation*, Eng. ed., p. 7) is of importance: "A special case of temperature radiation is the case of the chemical nature of the emitting substance being invariable. Nevertheless, *it is possible, according to what has been said, to have temperature radiation while chemical changes are taking place, provided the chemical condition is completely determined by the temperature.*"

According to the law of mass action the rate at which a body reacts is proportional to its active mass. Since the time of Guldberg and Waage it has been considered sufficient to regard the concentration of the substance as an accurate measure of the active mass, and this has been borne out by an accumulation of experimental results, which serve to demonstrate the general truth of the hypothesis. At the same time numerous facts are known which indicate that concentration *per se* is not the only factor determining reactivity. To attempt to extend the principle of mass action so as to allow for environment, it is necessary to take into account the energy exchanges which accompany, or rather precede, molecular change, for as the fact of a *finite* velocity demonstrates, all the molecules of a system are not at any one moment in the same reactive state. From what has already been said regarding the absorption of energy by an average molecule to bring its energy content to the critical value, it will be evident that the amount and nature of the radiation present in the system must play a definite part in the reactivity of a given species. From this point of view, therefore, the active mass of a species is not simply proportional to its concentration, but is simultaneously dependent on the radiational environment, the observed rate of reaction being due to the product of these two effects. The active mass may be, in the case of unimolecular decomposition, identical with the number of molecules brought per second into the reactive state by means of the radiation present in the system, or may be proportional to the number of molecules existing in the reactive

state. For multimolecular reactions it is undoubtedly true to say that the rate of chemical change is proportional to the product of the concentrations of the reactive molecules. The radiation hypothesis may be expressed in a sense by saying that the active mass of a species, spontaneously decomposing, is proportional to its concentration, multiplied by the radiation density of the type which the substance can absorb, the radiation being present in virtue of the temperature of the system. The radiation density, u_ν ,¹ is the amount of radiation corresponding with a certain frequency ν , which is present in unit volume of the system, when the radiation and the matter are in thermal equilibrium. If the radiation density is too small the substance will not react, howsoever great its concentration may be.

To say, however, that the reactivity of a given molecular species depends on its concentration and simultaneously on the density of the absorbable type of radiation present, in thermal equilibrium with the matter, may be inexact. The correct mode of expressing the radiation hypothesis depends upon whether reactive molecules exist or not in the case of a unimolecular process. If they do not exist, *i.e.* if they change into resultants immediately, then it would appear to be correct to say that the rate of reaction is directly proportional to the product of the concentration into the radiation density. If, on the other hand, the reactive molecules even in a unimolecular process do exist, *i.e.* if they possess a sensible life—as is necessarily the case when a multimolecular process is involved—the radiation hypothesis would be stated in a somewhat different form from that just given, namely, by making use of a postulate of Planck (*Theory of Heat Radiation*, English ed., p. 164) in connection with the relation of emission to non-emission by an oscillator, Planck's postulate being that *the ratio of the probability that no emission takes place (i.e. that the oscillator retains its energy) to the probability that emission does take place (i.e. that the oscillator loses its energy) is proportional to the radiation density u_ν of the frequency ν to which the oscillator responds.*

This ratio is given by ρu_ν , where ρ , the proportionality factor, is shown by Planck to be identical with $c^3/8\pi hn^3\nu^3$, c being the velocity of light in vacuo. Since u_ν itself is given by

$$\frac{8\pi hn^3\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1},$$

where k is the gas constant per molecule, it follows that—

$$\frac{\text{probability of no emission by oscillator}}{\text{probability of emission by oscillator}} = \rho u_\nu = \frac{1}{e^{h\nu/kT} - 1}.$$

Transferring this idea to the chemical case and identifying the

¹As already pointed out, u_ν has not the dimensions of energy density; the actual expression for energy density is $u_\nu d\nu$. The term u_ν may be called the radiation density factor.

reactive molecules with those which have not emitted (*i.e.* have retained) their abnormal energy we would write—

$$\frac{\text{number of reactive molecules}}{\text{number of unreactive molecules}} = e^{h\nu/kT}$$

The total number of molecules is the sum of the reactive and unreactive. Inverting the above expression, adding unity to both sides, and re-inverting, we obtain—

$$\frac{\text{number of reactive molecules}}{\text{total number of molecules}} = \frac{1}{e^{h\nu/kT} + 1} = e^{-h\nu/kT}$$

The application of the above postulate of Planck leads consequently to the relation :—

Concentration of reactive molecules = concentration of total molecules $\times e^{-h\nu/kT}$.

Writing the rate of reaction in the case of a *unimolecular* change as proportional to the concentration of reactive molecules, we get—

$$\text{rate of reaction} = \text{constant} \times \text{total concentration} \times e^{-h\nu/kT} \quad (1)$$

the constant being independent of temperature.

Similarly, in the case of a *bimolecular* reaction between two substances A and B, the rate of reaction is given by :—

$$\text{Constant} \times C_A \cdot C_B \times T^{1/2} \times e^{-h(\nu_A + \nu_B)/kT} \quad (2)$$

where $T^{1/2}$ has been introduced to allow for the variation with temperature of the average thermal speed of translation of the molecules in the case of a *gaseous* system. (In the case of a bimolecular reaction in solution the rate of collision depends upon the mobility or diffusion coefficients of the solutes, a quantity which varies much more rapidly with temperature than does the speed of translation of thermal motion itself.)

Equation (1) can be written in the form—

$$-dC/dt = k_0 C e^{-h\nu/kT}$$

where C stands for total concentration and k_0 for the constant independent of temperature. t stands for time.

Employing the ordinary expression for the rate of a unimolecular reaction on the basis of the law of mass action we have—

$$-dC/dt = k_{\text{obs.}} C,$$

where $k_{\text{obs.}}$ is the velocity constant determined by experiment. By combining the above two expressions it follows that—

$$k_{\text{obs.}} = k_0 e^{-h\nu/kT}$$

$$\text{or} \quad d \log k_{\text{obs.}}/dT = h\nu/kT^2 = N h\nu/RT^2 = \text{constant}/RT^2 \quad (3)$$

where N is the number of molecules in one gram-molecule.

This equation is identical in form with that of Arrhenius which is known to be in agreement with experiment for a great variety of reactions. It is by means of equation (3) that the position of a band head or frequency is calculated from the velocity constants observed at different temperatures.

Apart altogether from the radiation hypothesis and on a statistical basis Rice has shown (*loc. cit.* and also *Phil. Mag.*, **46**, 312, 1923) that for a unimolecular reaction the exact expression is—

$$d \log k_{\text{obs.}}/dT = (E + kT)/RT^2 \quad (4)$$

where E is the critical increment reckoned per gram-molecule. Combining equations (3) and (4) we obtain for a unimolecular process—

$$E + kT = Nh\nu$$

or as a close approximation in general—

$$E/N = h\nu \quad . \quad . \quad . \quad . \quad . \quad (5)$$

But E/N represents the amount of energy which has to be added to make a single molecule decompose. The above relation is therefore Einstein's law of the photochemical equivalent.

Although several investigations have been carried out to test Einstein's law for photochemical reactions (*cf.* Appendix VII.) very little has been done in connection with testing equation (5) for thermal reactions due to infra-red radiation. The case considered below is the decomposition of triethylsulphonium bromide in various solvents (*cf.* Taylor and Lewis, *J. Chem. Soc.*, **121**, 665, 1922).

Triethylsulphonium bromide has been shown by von Halban (*Zeitsch. physikal. Chem.*, **67**, 129, 1909) to decompose into ethyl bromide and di-ethyl sulphide in a unimolecular manner in various solvents. From von Halban's velocity constant data at different temperatures it is possible, by making use of the Marcellin-Rice equation, to calculate the critical increment per gram-molecule of the reactant. From this, assuming that one quantum is required per molecule, it is easy to calculate the frequency of the radiation which would accomplish this degree of activation. The calculated values of the frequency show that the triethylsulphonium bromide should exhibit an absorption band in the short infra region in the neighbourhood of 1μ , the precise location of the band depending upon the solvent employed. Using an infra-red spectrometer and radiomicrometer, Taylor and Lewis have observed the absorption spectra of triethylsulphonium bromide in the eight solvents employed by von Halban over the range 0.7μ to 3.6μ . The details of the procedure and measurements are given in the paper cited. It may be remarked that in general the solute is not very soluble, which renders it somewhat difficult in certain cases to determine the band, since this depends upon the difference in transmissive power of the pure solvent and the solution respectively. The results obtained are summarised in the following table :—

DECOMPOSITION OF TRIFTHYLSULPHONIUM BROMIDE

Solvent	Critical Increment, I _c (from von Halban's data) in cal. per mole	Wave length of Band Calculated from Value of I _c	Wave length Observed
Nitrobenzene . . .	28390	• 1.0μ	1.05μ
Tetrachloroethane . . .	31030	0.91	0.90
Propyl alcohol . . .	33960	0.84	0.89
Amyl alcohol . . .	33530	0.85	0.83
Benzyl alcohol . . .	36180	0.78	0.80
Acetic acid . . .	29220	0.97	0.90 0.95
Acetone . . .	{ 30450 } { 28560 }	2 0.96	1.3
Chloroform . . .	2 33320	2 0.85	1.0

It will be observed that in the first six cases the agreement between the calculated and observed wave-length of the band is satisfactory, thus affording a verification of equation (5). It is important in this case (in view of certain considerations dealt with later) to point out that no evidence was obtained from the absorption spectra curves over the range examined of the existence of bands at wave-lengths which are integral multiples of that quoted in the table. The bands referred to are the only ones observed due to the solute.

In the case of acetone and chloroform there is serious discrepancy between the observed and calculated positions of the bands. It is significant, however, that it is precisely in these two cases that von Halban observed abnormal behaviour on the part of the velocity "constants," this being attributed by him to the known fact that in acetone the triethylsulphonium bromide is ionised whilst in chloroform it is polymerised. The discrepancy, therefore, cannot be regarded as invalidating the relationship under consideration.

In the case of the inversion of sucrose there is also apparently satisfactory agreement between the observed and calculated positions of the absorption band (*cf.* Moir and H. A. Taylor, *Journ. Amer. Chem. Soc.*, **44**, 2886, 1922), as well as in the case of the conversion of γ -hydroxybutyric acid into the lactone (Garrett and Taylor, unpublished) and in the case of the hydrolysis of acetamide (Meehan unpublished). Further, it has been shown by Hojendahl (*Journ. Phys. Chem.*, 1924) that in the case of the transformation of fused maleic acid into fumaric, the critical increment obtained from velocity data corresponds to a wave-length 1.8μ. In agreement with this, Hojendahl has found that fused maleic acid exhibits an absorption band in the short infra-red region with its head at 1.8μ approximately.

Reference may also be made to certain results obtained by H. A. Taylor in connection with the anthracene dianthrane reaction in phenetol. From the velocity constant data of Luther and Weigert it can be calculated on the above basis that the dianthrane *de*-polymerises thermally owing to the absorption of radiation in the

neighbourhood of $707\mu\mu$. To test this Taylor exposed a solution of dianthrane to wave-lengths of this region—the isolation being carried out spectrographically and consequently with considerable loss in intensity—and obtained (for the first time) a true photo-*de*polymerisation of dianthrane in excess of the thermal effect. Exposure to wave-lengths of the same intensity in the neighbourhood of $600\mu\mu$ and $800\mu\mu$ respectively produced much less marked effect. (The above photodecomposition is naturally not to be confused with the photopolymerisation of anthracene itself which has been known for fifty years).

The Unimolecular Velocity Constant.

Whilst the radiation hypothesis as expressed in equation (5) accounts satisfactorily for the influence of temperature upon the velocity constant, it has not yet been shown that the hypothesis is capable of accounting for a velocity constant itself, although ultimately we cannot regard any theory as satisfactory or complete which is unable to permit of such calculation. The crucial case is the unimolecular type of reaction, and various attempts have been made to apply the radiation hypothesis to this case. It may be said at once that up to the present time (1923) the problem has not been solved satisfactorily. The nature of the difficulty encountered is dealt with by W. C. M. Lewis (*Phil. Mag.* [vi.], **39**, 26, 1920).

Briefly, the initial difficulty is the choice between the two possible modes of absorption of radiant energy by matter, namely the discontinuous and the continuous respectively. On Planck's first formulation of the quantum theory of radiation the act of absorption is regarded as discontinuous, *i.e.* in quanta of energy, which implies that radiant energy in free space is made up of discrete units, a view which Planck later gives reasons for relinquishing, although the conclusion is not devoid of uncertainty. The continuous view of absorption (which constitutes Planck's second formulation of the quantum theory) is the one which is adopted in the following considerations.

On the basis of the continuous or classic view of absorption, Planck has shown that the rate of absorption of radiation of frequency ν by an oscillator—here identified with the electron—is given by—

$$3m \cdot u_{\nu}$$

where e and m are the charge and mass of an electron, and u_{ν} , for the range of wave-lengths ordinarily involved in chemical change, is defined by—

$$u_{\nu} = \frac{8\pi h^3 \nu^3}{c^3} e^{-h\nu/kT}$$

where h is Planck's constant, c the velocity of light in a vacuum, and n is the refractive index.

If we now consider a gaseous system, containing N molecules, and

suppose that one valency electron per molecule is involved in the dissociation process, it is evident that the total amount of energy absorbed per second is—

$$\frac{8\pi^2e^2h\nu^3}{3mc^3} \cdot e^{-h\nu/kT} \cdot N.$$

If one quantum of energy, $h\nu$, is required by the valency electron for decomposition of the molecule, it follows that the number decomposed per second is the above quantity divided by $h\nu$, or—

$$\frac{8\pi^2e^2h^3\nu^2}{3mc^3} \cdot e^{-h\nu/kT} \cdot N$$

and hence the velocity constant of the unimolecular process is given by

$$k_{\text{uni}} = \frac{8\pi^2e^2h^3\nu^2}{3mc^3} \cdot e^{-h\nu/kT} \quad (6)$$

$$k_{\text{uni.}} = 2.465 \times 10^{-22} \cdot n^3\nu^2e^{-h\nu/kT}.$$

If the refractive index n is taken to refer to the whole gaseous system its value is very nearly unity. Taking the case of the unimolecular decomposition of phosphine measured by Trautz and Bhandarkar (*Zeitsch. anorg. Chem.*, **106**, 95, 1919) from the *observed* temperature coefficient the value of E and consequently of ν can be obtained. On substituting this value together with the appropriate value of T the unimolecular velocity constant of the decomposition of phosphine can be calculated by means of equation (6). It is found that this calculated value of k is only 10^{-7} of the observed value, that is, the discrepancy is enormous. A precisely similar discrepancy is found in the case of the unimolecular decomposition of nitrogen pentoxide investigated by Daniels and Johnston (*Journ. Amer. Chem. Soc.*, **43**, 53, 1921). In the latter case the exact factor, with which the calculated values of the velocity constant must be multiplied so as to make them identical with the observed, is 1.2×10^7 . This factor does not appear to vary with temperature.

On reviewing equation (6) it will be observed that the numerical value attributed to the refractive index n is unity. In the neighbourhood of a band the value is known to be somewhat higher, but the alteration usually regarded as legitimate would leave the discrepancy factor still enormous. In fact if the discrepancy is to be explained on the basis of an enhanced value for n it would be necessary to ascribe to n a value of the order 200, and further to assume that n maintains its value throughout the course of the reaction. As the original substance decomposes, however, we would expect the value of n to diminish, provided n refers to the decomposing gas substance as a whole. This difficulty *might* be overcome by assuming that the resultants of the reaction are just equally efficient in contributing to the refractive index, but this is not very probable. A more serious objection arises, however, if we consider the reacting system under different *initial* pressures. Since pressure is a determining factor for the refractive index of the

system as a whole the velocity constant would on this basis depend on the pressure. This, of course, would be contrary to the concept of unimolecular reactions. It seems quite impossible to attempt to account for the discrepancy on the basis of n , the refractive index term.

As regards the problem of applicability of the equation (6), three distinct views may be considered to be held at the present time (1923).

1. The radiation hypothesis of thermal chemical change may be regarded as invalid, the observed velocities being so much in excess of those required by the hypothesis. Whilst the concept of activation is retained the transfer of the necessary energy is attributed to collisions. That the radiation hypothesis is inadequate is the view of Lindemann (*loc. cit.* and *Phil. Mag.*, **40**, 671, 1920), Langmuir (*Journ. Amer. Chem. Soc.*, **42**, 2190, 1920) and of Christiansen and Kramers (*Zeitsch. physikal. Chem.*, **104**, 451, 1923).

Even though the radiation hypothesis were discarded it would still be quite logical to regard chemical kinetics as essentially quantisable. That is, it would be legitimate to calculate the position of an absorption band from the magnitude of the temperature coefficient of the reaction velocity constant, using the relation $E = h\nu$. All that has been shown in the foregoing is that the radiation hypothesis is (necessarily) in agreement with this relation.

2. The radiation hypothesis may be correct, but equation (6) may be an incorrect expression of the hypothesis, in the sense that the actual rate of absorption of energy may be much more rapid than is allowed for in the deduction of the equation. This view is considered briefly later in connection with the introduction by Rice of a dimensionless factor into equation (6), the physical basis for this factor being the assumption—suggested on other grounds—that the radiation field is not uniform but that in the immediate neighbourhood of matter (atomic systems) the radiation is as it were “condensed”.

3. The radiation hypothesis may be valid and equation (6) may be correct, but the experimental data in the case of unimolecular reactions in gases may be wholly unsuitable for testing equation (6) owing to the existence of powerful catalytic effects. We have to consider these various possibilities in a little more detail, taking the third possibility first.

The fact already mentioned that the discrepancy between experiment and equation (6) is almost identical for two unimolecular reactions as different as phosphine decomposition and nitrogen pentoxide decomposition suggests that the experimental data are valid. It has been found, however, by Hinshelwood and Topley (*J. Chem. Soc.*, **125**, 393, 1924) that the phosphine decomposition, even up to 1044° abs., is confined to the walls of the vessel, the reaction being therefore a typical example of heterogeneous catalysis. These authors also find that the critical increment is between 40,000 and 50,000 cal.¹ (and this value is constant),

¹ If this were characteristic of gaseous PH_3 in bulk the gas ought to be visibly coloured. So far as is known this is not the case.

result completely at variance with a value of the order 85,000 cal. obtained from the data of Trautz and Bhandarkar, this value being attributed by these authors to the homogeneous reaction which they regard as predominating at the higher temperature range (about 1000° abs.). If we accept Hinshelwood and Topley's value for the critical increment, equation (6) reproduces, at least in so far as order of magnitude is concerned, the velocity constant for the unimolecular reaction which occurs, however, in the surface layer.

Hinshelwood and Prichard (*Journ. Chem. Soc.*, **123**, 2725, 1923) have likewise shown that the decomposition of hydrogen peroxide vapour and the decomposition of sulphuryl chloride vapour are unimolecular reactions but occur at the surface of the vessel. In the case of sulphuryl chloride the authors give the critical increment as 35,000 cal. Inserting this in equation (6) for a temperature 556° abs. the velocity constant calculated (in secs.⁻¹) is 5.7×10^{-7} , whilst that observed is 2×10^{-3} , i.e. the observed is 4×10^3 times the calculated. In the light of this result little stress can be laid apparently on the approximate agreement obtained in the case of phosphine.

Again, as regards the decomposition of nitrogen pentoxide the recent observations of Daniels, Wulf and Karrer (*Journ. Amer. Chem. Soc.*, **44**, 2402, 1922) show that this reaction is not a simple spontaneous process but is very powerfully catalysed by a trace of nitrogen peroxide, itself one of the decomposition products. The authors have shown this to be the case by removing the nitrogen peroxide by means of ozone. [As Daniels, Wulf and Karrer point out, one of the striking things about the catalytic effect of NO₂ on the decomposition of nitrogen pentoxide is the fact that a mere trace of NO₂ is sufficient, any additional quantity being without further influence. Had this not been so the observed unimolecular velocity constant would not have been a satisfactory constant throughout a run, for NO₂ accumulates in the system as a result of the decomposition. This behaviour is so abnormal as to suggest that the true catalyst is some third substance, hitherto unidentified but present in minute amount which is in some way made effective by the nitrogen peroxide.] It must be remembered, however, that the critical increment employed in testing equation (6) is that obtained experimentally, i.e. for the catalysed process itself, and had this been analogous to the phosphine case the numerical discrepancy referred to should have disappeared in a like manner. Until this reaction has been studied in further detail it is impossible to say whether it constitutes evidence in favour of equation (6) or constitutes a definite disproof of this equation.

At the present time (1923) no really satisfactory unimolecular gaseous process occurring apart from catalytic effects is known.¹ In

¹ The significance of *polar* molecules acting as catalysts by union with a certain fraction of the otherwise inert "reactant" has been emphasised by Norrish (*Journ. Chem. Soc.*, **123**, 3006, 1923) in connection with the well-known retarding effect of desiccation and more particularly in connection with the effects produced by the nature of the walls of the containing vessel. Thus in the (bimolecular) reaction between bromine and ethylene Norrish has shown that when the wall consists of

view, however, of the possible invalidity of equation (6) other expressions which have been suggested must be considered briefly here.

Perrin in 1919 (*Annales de Physique*, Vol. II.) suggested that the velocity constant of a spontaneous process brought about by radiation could be represented by—

$$k_{\text{uni.}} = se^{-h\nu/k\tau}$$

where s denotes the sensitivity (*sensibilité*) of the system. This equation is of the same type as that already considered, but as s is not explicitly analysed it does not carry the problem any further.

Dushman (*Journ. Franklin Inst.*, **189**, 515, 1920) has suggested that the velocity constant is given by—

$$k_{\text{uni.}} = \nu e^{-h\nu/k\tau} \quad (6a)$$

where ν is the frequency of the radiation *apparently* responsible for the chemical change, ν being calculated from the temperature coefficient of the reaction, Einstein's photochemical law being assumed. Dushman's equation is, in the first place, empirical. It leads to values approximately 10^7 times that given by equation (6). Thus it applies to the decomposition of gaseous nitrogen peroxide (in the ordinary catalysed condition) in so far as order of magnitude is concerned, and of course its simplicity of form is attractive. The equation likewise applies to about the same extent to a dissolved gas, namely the decomposition of nitrogen pentoxide dissolved in chloroform and in carbon tetrachloride (*cf.* Lueck, *Journ. Amer. Chem. Soc.*, **44**, 757, 1922). On the other hand, it leads to velocity constants which are only of the order of one thousandth or less of those observed in the case of the decomposition of triethylsulphonium bromide in the various solvents referred to in a previous section. Dushman's equation is probably of too simple a form to apply to the decomposition of non-volatile solutes in solution.

Recently theoretical deductions of equations similar to that of Dushman have been offered by Rice and by McKeown (*Phil. Mag.*, **46**, August, 1923). Rice's method is based on statistical considerations which at a certain stage are quantised, the molecule being regarded as a simple mechanical one in which two bodies are imagined as bound together by a quasi-elastic force. The distance apart of these two bodies (atoms) is assumed to be capable of taking on any value from zero to infinity, the mutual potential energy of the two portions increasing until their distance apart attains a certain "critical" value, beyond which the potential energy either decreases or remains constant. When the "critical" position is reached dissociation of the molecule is supposed to have occurred.

The equation obtained by Rice is—

$$k_{\text{uni.}} = 2\nu e^{-h\nu/k\tau} \quad (6b)$$

(non-polar) paraffin wax the reaction is very slow compared with its rate when the wall is of glass or still more when it consists of the highly polar stearic acid. In such cases the point of interest is shifted but the problem of explaining the mode of initial activation still remains to be accounted for *quantitatively*.

for frequencies likely to be of significance for chemical change. If we compare this with equation (6) deduced on the basis of the rate of absorption of energy by a Planck oscillator, *viz.*

$$k_{\text{uni.}} = \frac{8\pi^2 e^2 n^3 v^2}{3mc^3} e^{-h\nu/kT}$$

we see that the ratio,

$$\frac{k_{\text{uni.}} (\text{Rice})}{k_{\text{uni.}} (\text{Planck})} = \frac{1}{2\pi^2 n^3} \cdot \frac{3mc^3}{2e^2} \cdot \frac{c}{v} = \frac{1}{2\pi^2 n^3} \cdot \frac{3mc^3}{2e^2} \cdot \lambda.$$

where λ is the wave-length. But r , the radius of the electron, is given by $\frac{2}{3} \frac{e^2}{mc^2}$, so that,

$$\frac{k_{\text{uni.}} (\text{Rice})}{k_{\text{uni.}} (\text{Planck})} = \frac{\lambda}{2\pi^2 n^3 r}$$

In connection with the above result Rice comments as follows:—It is becoming more and more doubtful if the behaviour of a substance towards radiation of a frequency corresponding to any of its bands of absorption can be adequately treated by the methods of classical theory, based as they are on the postulate of the transmission of continuous coherent waves. Physicists are coming gradually to the view that for a considerable body of phenomena (and just those where absorption or production of radiation is concerned) the assumption of the propagation of discrete elements of energy is necessary. On the other hand, the facts of interference and polarisation necessitate the retention of some features of the old wave theory. Now the phenomena require for their clearest manifestation the condition that the interfering beams should be almost ideally monochromatic, *i.e.* that the range of frequencies involved should be extremely narrow. Under such circumstances interference has been shown with a path difference several hundred thousands of wave-lengths between the two beams. This would point to the conclusion that under such circumstances a quantum of such radiation would possess a length equal to such a number of wave-lengths. Also the facts concerning the dependence of resolving power on aperture would seem to show that a quantum "can fill a telescope". Now it is a well-known result of Fourier analysis that such a beam, with its close approximation to monochromatism, can be represented by a succession of wave-trains, each train consisting of a great number of waves whose amplitudes gradually decrease from the middle of the train towards the front and the rear, with a space practically free from movement between each train. On the other hand, a beam whose approach to monochromatism was less perfect would be represented by a train of fewer waves with a quiescent space between. Indeed where the range of frequencies was sufficiently great a single wave with a few minute ripples in front and behind represents a wave train with sufficient accuracy. Thus, whereas in certain circumstances a quantum of energy may possess a relatively great length (the "coherence length" of the wave) and great sectional area; under other circumstances its length might be comparable with one wave-length and its sectional area also reduced, *viz.*, when the range of frequencies involved is relatively large. Further, if the quantum is capable of being absorbed by an electron it would seem natural to assume that its sectional area is of the order of the square of the electronic radius.

Referring now to the ratio of the two rates of absorption of energy given above, a physical basis would be found for the ratio λ/r if the energy around the binding electron involved in the reaction were "condensed" or concentrated in a ratio comparable with λ/r as compared with the energy in the vacuous hohlraum at the same temperature. Such a condensation would appear to be a possibility on the views expressed above. A quantum of energy with a length comparable with λ and a section whose linear dimensions are comparable with r would encounter an

electron. If its frequency range found no "sympathetic" frequency in the electron it would rebound with only a small change in energy and frequency. If the frequencies agreed sufficiently there would be absorption, and as a preliminary to such absorption the energy would condense into a volume comparable with the size of the electron itself. This would involve a concentration of energy in and immediately around the electron of the amount suggested by the comparison of the two formulæ for velocity constants. This would, of course, denude the inter-electronic space of its energy; but there appears to be no contradiction of the law of conservation as the walls and material present can supply the necessary total energy involved in the reaction.

In Rice's deduction the quantisation treatment is that of Planck, in which all physical states corresponding to points in the phase extension diagram are regarded as possible. This differs sharply from the concept—made familiar in the Bohr theory—of stationary states in which only the points on the region *boundaries* of the representative space represent physically possible states. The concept of such stationary states lies at the basis of McKeown's method which is based on a direct application of Einstein's treatment of the generalised Bohr model (*cf.* Chap. V.). On the latter basis the equation actually found is—

$$k_{n \rightarrow m} = \frac{p_m}{p_n} \cdot \nu \cdot e^{-h\nu/kT} \quad (6c)$$

where p_m and p_n are the *a priori* probabilities of the states m and n respectively, using the term in the sense of Sommerfeld. n denotes the normal state, m the activated state of the molecule. (The *a priori* probabilities take account of the fact that each quantum state of definite energy content of a molecule may be realised in different ways, the p 's representing the number of possible modes of realisation of each state.)

The equation of McKeown differs from that of Dushman only in the factor p_m/p_n which may be greater or less than unity. For Bohr orbits in the generalised Sommerfeld sense, p_m would be greater than p_n , but in no case would p_m/p_n be a large numerical factor.

It is necessary to point out that McKeown's result is obtained primarily on the assumption that the life of a stationary state m , is equal, in the absence of radiation, to the period $1/\nu$ which characterises the transitions $n \rightleftharpoons m$ (*cf.* footnote, however). McKeown points out that the corresponding rate of absorption from a radiation field is very much greater than that given by classical electrodynamics.¹ Once more, if we

¹ This follows from the mode of deduction of equation (6c). We are considering a molecule capable of existing in a discrete series of states. The normal state (in respect of energy content) is denoted by n , the chemically active state by m . Following Einstein (*Physikal. Zeitsch.*, 18, 121, 1917) the probabilities of the transitions $n \rightarrow m$ and $m \rightarrow n$ in the time interval dt are—

$$\frac{d\pi}{n \rightarrow m} = B_n^m u_\nu dt, \quad \text{and} \quad \frac{d\pi}{m \rightarrow n} = (A_m^n + B_m^n u_\nu) dt$$

where u_ν is the radiation density factor for the frequency ν corresponding to the changes $n \rightleftharpoons m$, and the A and B terms are probability factors.

Writing $A_m^n/B_m^n = K$, Einstein shows that $K = 8\pi h n_0^3 \nu^3 / c^3$ (where n_0 in this formula denotes refractive index), and that $B_n^m = B_m^n$. McKeown now assumes that

are to retain the electrodynamic expression, it is necessary to assume a high condensation of radiation in the immediate neighbourhood of particles of matter.

The radiation hypothesis of thermal change has been criticised adversely, *cf.* Langmuir (*Journ. Amer. Chem. Soc.*, **42**, 2190, 1920). A good deal of the criticism is based on an inadequate differentiation between thermal conditions and photochemical conditions, a point which is considered later. Langmuir has, however, emphasised that in the case of phosphine—Langmuir necessarily deals with the older data of Trautz, but the argument still appears cogent even for the newer data—(and it may be added in the case of nitrogen pentoxide) no absorption band is exhibited by the gas at the wave-length region calculated from the E term by equating E to one quantum of energy of frequency ν . This possibly necessitates a modification of the simple view that a single quantum is required per molecule, and it appears necessary in certain cases to substitute for the single quantum of relatively high frequency ν a limited number of quanta corresponding to a lower frequency or longer wave-length which the substance is actually capable of absorbing.

In the case of the unimolecular decomposition of nitrogen pentoxide investigated by Daniels and Johnston (*loc. cit.*) the observed critical increment corresponds (when equated to one quantum per molecule decomposed) to the wave-length 1.13μ . Daniels and Johnston have found that nitrogen pentoxide is not decomposed photochemically by exposure of the system to an external illumination of this wave-length nor is there any evidence at the present time that this gas possesses an absorption band at this region. On the other hand, the frequency corresponding to the wave-length 1.13μ is exactly three times the frequency corresponding to one of the known infra-red absorption bands exhibited by N_2O_5 according to the measurements of Warburg and Leithauser (*Ann. Physik* [iv.], **28**, 313, 1909). It may be concluded therefore that the thermal process is brought about by the radiation belonging to the longer wave-length and that the critical increment per molecule is made up of three quanta of the lower frequency type. That simple integral multiples may be expected in general would follow from Baly's analyses of absorption spectra (*vide supra*).

A, which denotes the probability of the spontaneous change $m \rightarrow n$, may be written as equal to ν , the characteristic frequency of the change. (Physically this means that the life of the stationary state m is equal, in the absence of radiation, to the period $1/\nu$.) Consequently $B_n^m = B_m^n = c^3/8\pi h\nu^2 n_0^3$. But the rate of absorption of radiant energy for the change $m \rightarrow n$ is $h\nu B_n^m u_\nu$ per molecule $= h\nu^2 e^{-h\nu/kT}$. The numerical value of this is about 10^7 times that given on the basis of the expression of Planck, viz.—

$$\frac{\pi c^2}{3m} u_\nu = \frac{8\pi^2 c^2 h n_0^3}{3mc^3} e^{-h\nu/kT}.$$

It must be pointed out, however, that according to Kramers (as a consequence of the correspondence principle) the life of the stationary state is considerably greater than $1/\nu$ and that in fact the Bohr treatment should lead to a result in agreement with equation (6).

In view of such results it is necessary to allow for the substitution of several quanta of relatively low frequency in place of a single quantum of relatively high frequency in the expression for the velocity constant. This may be effected in equation (6) as follows. Let us take the case in which the critical increment is made up of 3 quanta of frequency ν_1 . In a stationary statistical state of the system the number N_2 of molecules each containing *two* of such quanta is given by—

$$N_2 = N(1 - e^{-h\nu_1/kT})e^{-2h\nu_1/kT} = Ne^{-2h\nu_1/kT}$$

very nearly. N stands for the total number of molecules. (This expression for N_2 may be obtained by considering the expression for M , the number of molecules having zero energy given in Chap. II. The expression is also given by Planck (*Sitzungsber. Preuss. Akad.*, p. 923, 1914).) The mechanism of the unimolecular change may now be identified with the absorption of *one* quantum $h\nu_1$ by those molecules which already contain two quanta of this type. Hence, as before, the total energy absorbed per second is—

$$\frac{8\pi^2c^2h\nu_1^3}{3mc^3}e^{-h\nu_1/kT} \times Ne^{-2h\nu_1/kT}.$$

The number of molecules decomposed per second is given by—

$$\frac{8\pi^2c^2h\nu_1^3}{3mc^3}e^{-3h\nu_1/kT} \cdot N$$

whence,

$$k_{\text{uni.}} = \frac{8\pi^2c^2h\nu_1^3}{3mc^3}e^{-3h\nu_1/kT}$$

That is, the velocity constant is $1/(3)^2$ or 1/9th of that calculated on the basis that one quantum $h\nu$ (where $\nu = 3\nu_1$) brings about the required activation. In general if $\nu = p\nu_1$, the resulting velocity constant is $1/p^2$ of the value which would be obtained had the decomposition actually been brought about by the absorption per molecule of *one* quantum of frequency ν .

The Bimolecular Velocity Constant.

For the case of bimolecular reactions it is only necessary to remind the reader of what has been said earlier, namely that the rate depends on the collision frequency between molecules in the active or reactive state, this state having been attained owing to absorption of radiation. The rate of activation is itself a unimolecular process, but such rate is extremely great, in general, owing to the relatively low value of the critical increment. If the system consists of molecules of two substances A and B the active fraction of the A molecules is given by $e^{-E_A/RT}$, the active fraction of the B molecules by $e^{-E_B/RT}$. The observed rate of the bimolecular process is proportional to $C_A C_B e^{-(E_A + E_B)/RT}$. For *gaseous* reactions the proportionality factor is calculable on the basis of kinetic theory and the observed rate quantitatively accounted for (*cf.* Lewis, *Journ. Chem. Soc.*, **113**, 471, 1918). The bimolecular velocity constant

in a gaseous system, the constant being expressed in gram-molecules per litre per second, is given by—

$$k_{bi} = 3.8 \times 10^{21} \times \sigma_{AB}^2 \times \sqrt{u_1^2 + u_2^2} \times e^{-(E_A + E_B)/RT} \quad (7)$$

where σ_{AB} denotes the range¹ of nearest approach of the centres of the A and B molecules in a collision, the terms u_1 and u_2 denoting the root-mean-square velocities of translation of the molecules of A and B respectively at the temperature T.

It is an experimental fact that the total observed critical increment in the case of bimolecular reactions (which proceed at a measurable rate at ordinary temperatures) is usually between 10,000 and 20,000 cal., this representing the sum of the individual critical increments E_A and E_B . Consequently these individual quantities must be lower in general than the critical increment of a unimolecular process which proceeds at a measurable rate, for this is known to possess at least as high an E value as the *total* E of the bimolecular case. This justifies the statement made above that the equilibrium amounts of the active molecules of both A and B are attained rapidly compared with the rate of the subsequent bimolecular process.

It has already been stated that the frequency actually responsible for the activation of a given molecular species may be a sub-multiple of the frequency which would be calculated directly from the critical increment. In other words, instead of one quantum effecting the decomposition or activation, more than one quantum, *i.e.* a *few* quanta, of correspondingly lower frequency may be actually involved in bringing about the change. We have already discussed this in connection with unimolecular processes. In these cases the substitution of two quanta in place of one (larger) quantum results in a slower speed than would have been obtained if the change had actually been effected by the larger single quantum.

In the case of certain bimolecular processes it is also to be anticipated that activation will be effected by absorption by a few quanta per molecule in place of a single (correspondingly larger) quantum. This, however, does not affect the observed speed of the bimolecular reaction; it affects the rate at which the active forms are produced, but since this is very much greater than the observed speed the latter is left unaffected. That activation may be brought about by the absorption of a few quanta in place of one can, however, be shown from a comparison of critical increments with absorption spectra. The only instance so far known in the case of gaseous bimolecular reactions is the *thermal* decomposition of ozone according to the equation:—



¹ The quantity σ_{AB} is related to the individual radii of the A and B molecules by the expression—

$$\sigma_{AB} = (\sigma_A + \sigma_B)/2,$$

where σ_A and σ_B denote the individual radii.

This reaction proceeds at a measurable velocity at relatively low temperatures such as 100° C. Under these conditions it has been shown by Warburg (*Ann. Physik* [iv.], **9**, 1286, 1902), by Clement (*ibid.*, **14**, 342, 1904), and by Chapman and Jones (*Journ. Chem. Soc.*, **97**, 2463, 1910) that the decomposition is truly bimolecular. Applying the equation for bimolecular reaction velocities in gases, *viz.* equation (7), it is possible to calculate the value of the exponential term, namely $e^{-2E/RT}$, which appears in the velocity expression, by making use of the experimental data of Chapman and Jones. The term E stands for the critical increment of *one* gram-molecule of ozone in respect of the bimolecular change. Since two molecules are involved simultaneously the total critical increment which partly defines the speed of the reaction is $2E$. It is thus found that $E = 11,800$ cal. The accuracy of this quantity depends mainly upon the degree of accuracy of the value adopted for the range of approach in a collision between two ozone molecules. This value of E agrees satisfactorily with that determined experimentally by Clement, namely $2E = 26,000$ cal. and therefore $E = 13,000$ cal. The wave-length corresponding to $E = 13,000$ cal. is 2.17μ , that corresponding to $E = 11,800$ is 2.40μ ; that is the activation belongs to the short infra-red region. It is worthy of note that according to Warburg and Leithauser (*Ann. Physik* [iv.], **28**, 313, 1909) ozone possesses a characteristic absorption band in the short infra-red with its head at 4.756μ . This is approximately double the wave-length or half the frequency obtained from a consideration of Chapman and Jones' velocity data, and indicates that probably two quanta of the 4.756μ type are involved in the activation of each ozone molecule, which must take place before the bimolecular process becomes possible. Naturally this degree of activation is only a partial one. To bring about the unimolecular decomposition of ozone, that is to dissociate the ozone molecule into a molecule of oxygen and an atom of oxygen, as a minimum a quantum of energy corresponding to the red end of the *visible* region is necessary (*cf.* Griffith and Shutt, *Journ. Chem. Soc.*, **119**, 1948, 1921).

Catalysis in Homogeneous Systems.

On examining the expression obtained on the basis of the radiation hypothesis for the reaction velocity of a *unimolecular* process it becomes evident that the controlling term is the exponential, and that the smaller the critical increment, that is, the smaller the effective frequency the greater is the velocity. Consequently, on the radiation hypothesis it would be concluded that if some environmental influence, such as a solvent, alters the mode of vibration of the atoms or electrons involved in the chemical stability of the molecule (probably as a result of union of solute and solvent) in such a way as to decrease the frequency, then such a solvent will act as a positive catalyst with respect to some standard solvent condition taken for comparison. As a corollary it would follow that a *positive* catalyst, of the *environmental* or *solvent* type

(and of this type only), must *diminish* the temperature coefficient of the reaction—since the temperature coefficient depends on the magnitude of the critical increment—and conversely, a *negative* catalyst of the *same type* will *increase* the temperature coefficient.

Let us now consider the case of a bimolecular reaction. As before the magnitude of the critical increment and therefore of the vibration frequency will depend upon the nature of the solvent. The rate, however, depends not only upon the magnitude of the critical increment but also upon a collisional term covered by the product of the concentrations of the reactants and certain other quantities. One of these concentration terms may be a *solute* catalyst itself and consequently a catalytic effect may be produced quite apart from a variation in the critical increment. The statement that a catalyst functions by affecting the critical increment—a positive catalyst lowering the temperature coefficient, whilst a negative catalyst raises it—must be restricted to a particular type of catalysis, namely the solvent or environmental type. This restriction is so important that it is necessary to discuss homogeneous catalysis in a little more detail in order to emphasise it.

The term catalysis as usually employed is a comprehensive one, including non-stoichiometric effects as well as stoichiometric. As examples of the latter we have reactions brought about by ions and molecules of solutes in homogeneous solutions: non-stoichiometric catalysis being found in the influence of the solvent, in the case of homogeneous solutions, and by the surface in heterogeneous systems.

The intermediate compound view of catalysis, which has been very generally accepted and for which there is much experimental evidence, is not a general theory of catalysis as a whole. It applies essentially to stoichiometric catalysis with a possible extension to heterogeneous catalysis in which it is difficult and perhaps unnecessary to draw a sharp distinction between adsorption and temporary chemical combination.

In the case of stoichiometric catalysis in homogeneous systems the intermediate compound view affords an explanation of one aspect of the phenomenon, namely, the purely *material* mechanism of the process. It serves, in short, to bring such catalytic reactions into the category of ordinary stoichiometric processes, to which we would not apply the term catalytic. It cannot do more than this. The further theoretical treatment of stoichiometric catalysis becomes identical with that which must be applied to stoichiometric *non-catalytic* processes.

The characteristic feature of positive catalysis is the usually enormous increase in velocity brought about by the presence of the catalyst. On the basis of the intermediate compound theory this is due to the formation of entities which, in the absence of the catalyst, are either not produced at all or at most in minute amounts. The increase in speed is attributed directly to the greatly increased concentration of reacting individuals. Whilst this is undoubtedly true for stoichiometric catalysis no similar treatment seems adequate for non-stoichiometric catalysis. The explanation of the latter type cannot be found in material consideration alone, nor indeed can stoichiometric catalysis be *completely*

stated in such terms; it is necessary to consider the energy changes involved as a preliminary to the observed material changes.

In the light of what has been said above it may be concluded that *in non-stoichiometric catalysis (solvent catalysis) the alterations in the observed velocity are due essentially to alterations in the critical increment; in stoichiometric catalysis (solute catalysis) the increase in velocity is due not to a change in the critical increment, but to a change in the concentration product upon which the exponential is multiplied.* (Naturally if so much solute catalyst is added that the nature of the medium is likewise altered there will be a change in the critical increment at the same time. This behaviour may be looked for in reactions between substances composing a liquid mixture, as distinct from a reaction in a dilute solution.)

That stoichiometric catalysis, *e.g.* catalysis by means of ions, involves no sensible change in the critical increment, is shown by the results obtained in the inversion of sucrose under the agency of hydrogen ions, this process having been shown to be a bimolecular one involving the hydrogen ion as one of the reactants (*cf.* Moran and Lewis, *Journ. Chem. Soc.*, **121**, 1613, 1922).

INVERSION OF SUCROSE (20 PER CENT. SOLUTION)

Conc. of HCl.	Mean Velocity Constant $\times 10^3$			$k_{35^\circ}/k_{25^\circ}$	$k_{45^\circ}/k_{25^\circ}$
	at 25° C.	at 35° C.	at 45° C.		
0.0502 N	0.4169	1.738	6.213	4.17	3.57
0.2512	2.255	9.355	35.86	1.14	3.83
0.4137	4.043	17.00	60.62	4.20	3.57
0.900	11.16	46.76	148.8	4.19	3.18
1.214	17.45	75.97		4.35	

The variations in the value of the temperature coefficient over a given range of temperature are irregular and not large; at the same time the velocity constant increases over forty-fold, due to the increase in the concentration of the acid. It is evident that the increase in the velocity is not due to any sensible change in the critical increment (which can be calculated from the temperature coefficient), but to the production of higher concentrations of reactants possessing approximately a constant critical increment.

It is of interest to contrast the relative independence of the value of the critical increment, E , in respect of concentration of the solute catalyst, *e.g.* the hydrogen ion, with the marked variation in E produced by altering the nature of the solvent. The data of von Halban on the decomposition of triethylsulphonium bromide in various solvents, already cited, is a case in point. Analogous results have been obtained by Dimroth (*Lieb. Ann.*, **373**, 336, 1910) on the decomposition of the methyl ester of benzyl-5-hydroxy-1, 2, 3. triazole carboxylic acid,

Further, the measurements of Cox (*Journ. Chem. Soc.*, **119**, 142, 1921) on the addition of aniline to bromoacetophenone (a bimolecular process) show a similar effect. A selection from data obtained by Cox is as follows:—

Solvent.	E in calories.
Benzene	8,088
Chloroform	10,760
Nitrobenzene	13,470
Ethyl alcohol	13,910
Benzyl alcohol	14,290

Whilst emphasising the influence of the solvent on the value of E it is not intended to convey the impression that addition compounds involving the solvent are absent. To simply postulate their existence, however, cannot be a satisfactory explanation of solvent catalysis.

In connection with solvent catalysis—as distinct from solute catalysis—which, according to the view expressed above, has its origin in an alteration in the E term, it would be concluded that for a given reaction the greater the E value (*i.e.* the greater the temperature coefficient), the smaller the velocity constant, at a given temperature. This conclusion is borne out in a number of cases but is not general.

The conclusion holds for the decomposition of triethylsulphonium bromide in the solvents cited in the following table. The temperature selected is 50° C., since velocity measurements have been made at this temperature by von Halban in the case of the solvents, nitrobenzene, tetrachloroethane, and amyl alcohol. The value quoted for propyl alcohol is extrapolated from the lowest observed temperature, namely, 60° C., by the aid of the critical increment. Over this small range the extrapolation is sufficiently exact.

DECOMPOSITION OF TRIETHYLSULPHONIUM BROMIDE.

Solvent.	Velocity Constant.	Critical Increment.
Nitrobenzene	0.00145	28,390
Tetrachloroethane	0.00134	31,030
Amyl alcohol	0.000218	33,530
Propyl alcohol	0.000088	33,960

Although these velocity constants decrease as the E value increases, it will be observed—contrary to what would be expected on the basis of the statement made above—that the velocity constants are not related to one another simply in terms of the E values. Other factors are operative, *e.g.* possibly solvate formation to different extents in the different cases, in addition to differences in the refractive index which appears in the term multiplied upon the exponential (if the equation (6) be used), with the result that the velocity data as they stand are not strictly comparable. This means that the total solvent effect is not stated completely in terms of E, although this is usually the most

significant factor. This modification must therefore be introduced into the too greatly simplified statement made earlier in connection with solvent catalysis.

That the influence of the E term (as determining the relative values of the velocity constants) may be over-ridden is shown by the above (unimolecular) reaction, when occurring in the two solvents, benzyl alcohol and acetic acid respectively. The experimental data refer to 90°C .

DECOMPOSITION OF TRIETHYLSULPHONIUM BROMIDE.

Solvent.	Velocity Constant.	Critical Increment.
Benzyl alcohol .	0.00159	36,180
Acetic acid .	0.00080	29,220

In these cases the higher E value accompanies the higher velocity constant, in direct contradiction to the conclusion drawn above. This is presumably a further, and more extreme, illustration of the lack of comparability already referred to between variations in E and variations in velocity constant.

A similar deviation from what might be anticipated has been observed in bimolecular reactions. Thus Cox (*loc. cit.*) has obtained the following results in the case of the reaction between aniline and bromoacetophenone :—

UNION OF ANILINE AND BROMOACETOPHENONE.

k at 37.8°C .

Benzene . .	8,088	0.000985
Chloroform .	10,760	0.00186
Nitrobenzene .	13,470	0.0135
Acetone . .	11,080	0.0269
Benzyl alcohol .	14,290	0.0440
<i>n</i> -Butyl alcohol	14,060	0.0550
Ethyl alcohol .	13,910	0.0626
Methyl alcohol	12,440	0.0748

Attention may be called to the fact that the experimental values of velocity constants in the case of reactions in solution indicate the existence of what might be termed a "kinetic transition temperature" below which the rule, that the higher E value accompanies the smaller velocity constant, holds good, but above which the reverse relation applies. We are here considering a given reaction occurring in two different solvents at the same temperature. An illustration is afforded by Cox's measurements of the rate of union of aniline and bromoacetophenone. Taking the case of the two solvents, chloroform and benzene, and extrapolating the velocity constant temperature curves, it is found that a

"transition point" exists about 280° abs., whilst for the solvents acetone and benzyl alcohol there is "transition" at about 290° abs. At this point the two velocity constant curves cut one another. Below these temperatures the relation of E to k is in agreement with the rule that the smaller k accompanies the greater E . The theory embodied in the equations which precede would lead us to expect that the k values would tend towards the same asymptotic limit, but actual intersection would not be expected. It seems necessary to conclude that the E values are not really constant but are affected by additional as yet unrecognised factors, such, for example, as the possible influence of a change in dielectric constant with temperature on the part of the solvent, or change in degree of solvation or polymerisation with temperature. At the present time (1923) we are not in a position to bring velocity constant data into quantitative relation with the magnitude of the critical increment.

Thermal and Photochemical Change; the Thermionic and Photo-electric Effects.

These four effects, each of which has been considered already in some detail, bear a certain relationship to one another and it is necessary to consider precisely what this relationship is. Let us consider, in the first place, thermal and photochemical change.

Between these two conditions there is a resemblance and likewise a clear distinction. That both kinds of processes are attributed to radiation constitutes the resemblance. The distinction enters in the manner and extent to which the transformation of radiant energy occurs.

In the photochemical case, as ordinarily carried out, a material system, at a relatively low temperature, is exposed to the radiation emanating from a source of external radiation which possesses a certain area and is at a relatively high temperature. Under photochemical conditions, therefore, high temperature radiation acts upon low temperature matter. As a consequence, the phenomenon denoted by the term coefficient of absorption enters, the evaluation of the coefficient requiring information regarding the thickness of the layer passed through by the light. The existence of an absorption coefficient implies a *directed* radiational effect and the chemical changes produced by the light vary in different portions of the material system. The nature of the absorption is complex. Part of the light is absorbed and degraded into longer wave radiation with a consequent average increase in temperature of the material system. The system attempts, as it were, to attain the temperature of the light source. This purely physical absorption seems to constitute in general nearly the whole of the observed absorption. There is in addition, however, the chemical absorption to be considered (when chemical change is possible), in which a part of the absorbed radiation is converted into chemical change. According to Weigert (*Ahrens Sammlung*, **17**, 178, 1912), in the case of the photopolymerisation of anthracene in phenetole solution, of the

total amount of radiation absorbed only 4.5 per cent. is converted into chemical change. Further, if approximately monochromatic radiation from an external source passes through a material system it may be diminished in intensity and eventually extinguished, *i.e.* reduced to the intensity characteristic of the wave-length concerned in a black body space at the temperature of the material. The intensity cannot fall below this. The photochemical change brought about by radiation from an external source must depend upon the term $E_e dv$, which measures the rate of emission from the surface of the source.

On the other hand, thermal change, on the radiation hypothesis, depends upon the energy density of the radiation of the wave-length, which can be selectively absorbed by the material throughout the material system itself. That is, thermal changes depend upon $u_e dv$, and, further, the temperature of the radiation is identical with that of the matter. There is no directed effect comparable with that which is so characteristic of photochemical change. There is consequently no net absorption *coefficient* determinable from measurements at various positions; in other words, the amount of chemical change is independent of the special configuration of the volume. Owing to the identity of the temperature of the radiation and of the matter there is no net *physical* absorption such as that met with in the photochemical case. The net absorption or removal of radiation is entirely confined to the production of chemical change. The act of chemical change is, in fact, equivalent to a diminution in the radiation density of a certain wave-length, namely, that which the substance selectively absorbs. Such diminution is, however, made good at the expense of *all* the other wave-lengths constituting the entire spectrum which characterises a black body space at the temperature in question. Such adjustment is supposed to be rapid compared with the speed of the chemical change itself, so that at no instant does the distribution of energy among the different wave-lengths differ sensibly from that of a black ¹ space. If the reaction is, as a *whole*, endothermic, radiant energy passes in from the thermostat and the reaction proceeds at a constant temperature. The reverse happens in the case of a reaction which is, on the *whole*, exothermic. The radiation hypothesis has so far only been applied to processes which can be made to occur in a sensibly isothermal manner. In spite of the fact, therefore, that the chemical change may be brought about by monochromatic radiation, it follows from the above that the entire range of wave-lengths from 0 to ∞ is potentially available for the chemical change, owing to the radiation as a whole being at one temperature which is likewise that of the matter. The supply of effective radiation energy is therefore proportional to $\int_0^\infty u_e dv$. It will be observed that no analogue of this exists in the photochemical

¹ In using the term black body space it is to be remembered that the black body space imagined is supposed to possess the same refractive index for each wave-length as is actually possessed by the material in question. This factor will vary from one material to another.

conditions, in which, when the monochromatic radiation is itself exhausted, the chemical process likewise stops—the photochemical process here considered being one which goes very slowly under thermal conditions. In the above respect, instead of the thermal and photochemical conditions being analogous, they are in fact in sharp contrast, for in the thermal case the approximately monochromatic radiation which is being removed by the chemical change is made good at the expense of all the other frequencies, whilst in the photochemical case the approximately monochromatic radiation impinging on the system tends to be converted into radiation of all frequencies (physical absorption) the temperature of which is much lower than that of the initial beam. (Transformation of radiation of one wave-length into another or others cannot take place unless matter is present, *i.e.* through the intermediary of oscillators by means of repeated absorptions and reflections. No clear view regarding the actual mechanism of this has as yet been formulated.)

The distinction between the thermal occurrence of a unimolecular process in a gaseous system and the photochemical occurrence may be shown by considering the fractional number of molecules decomposed per second.

Under thermal conditions this quantity is the velocity constant k itself, which is given on different formulations of the radiation hypothesis by equations (6), (6*b*) or (6*c*).

In the photochemical case (even where the effective wave-length is the same as in the thermal case) it is necessary to consider a certain layer, say that most contiguous to the wall of the vessel on which the light from an external source impinges. Suppose the thickness of this layer to be dx , its cross section being one square cm., the temperature of the gas being T . Then the number of molecules within this selected layer is given by pdx/kT , where p denotes the pressure of the gas in absolute units. Considering the action due to the emission from one square cm. of a black body at the temperature T_1 , the total energy of frequency ν absorbed per second is $2aE_\nu d\nu dx$ (*cf.* Langmuir, *loc. cit.*), where a is the total absorption coefficient of light of frequency ν (actually of light lying between narrow frequency limits), E_ν is the intensity of the radiation entering the layer. The *chemically* effective energy absorbed is a small fraction, γ , of the total quantity absorbed, that is, the chemically effective energy absorbed per second is $2a\gamma E_\nu d\nu dx$, which from Planck's definition of E_ν for a region of the spectrum in which ν is sufficiently large (namely, the very short infra-red, the visible or ultra-violet), becomes :—

$$\frac{4\pi a\gamma h\nu^3}{c^2} e^{-h\nu/kT_1} d\nu \cdot dx.$$

This energy intake divided by $h\nu$ gives the number of molecules decomposed per second as

$$\frac{4\pi a\gamma \nu^2}{c^2} e^{-h\nu/kT_1} d\nu \cdot dx$$

Since the total number of molecules in the layer is pdx/kT it follows that the fractional number of molecules decomposed in the layer per second is

$$\frac{4\pi\alpha\gamma\nu^2kT}{c^2p} \cdot e^{-h\nu/kT_1} d\nu.$$

Apart from the presence of the $d\nu$ term the fundamental distinction between this expression and those given for thermal change is the presence of the term T_1 instead of T in the exponential. Owing to this the terms $\alpha\gamma$ make their appearance.

We have now to consider the photo-electric and thermionic effects respectively. In the first, the electrons are emitted from a material owing to exposure of the surface to radiation from an external source at a relatively high temperature and usually of relatively short wave-length. The thermionic effect is the emission of electrons due to the temperature of the material itself and consequently due to the radiation density of all wave-lengths characteristic of the temperature of the material. It is obvious that the photo-electric effect is the true analogue of photo-chemical change, the thermionic effect being the analogue of thermal chemical change. According to Langmuir (*loc. cit.*), the number of electrons emitted thermionically from a body at temperature T is of the order 10^6 times the number which can be emitted by the photo-electric effect of black body radiation of temperature T acting on a relatively cold material. On the above basis one would expect the photo-electric effect, if this is more than "skin deep," to involve such absorption terms as are represented by the product $\alpha\gamma$ which appears in the photo-chemical case, whilst these terms should be absent from the expression for thermionic emission. Richards' thermionic equation already discussed, leads to a relationship identical in form with that of Arrhenius or of Marcelin and Rice.

CHAPTER VIII.

Energetics of the ionic crystal lattice, and the affinity of atoms for electrons—The molecular crystal lattice—Molecular and atomic magnetic forces.

The Ionic Lattice.

THE elucidation of the structure of crystals by the X-ray method has led to investigation of the mechanics of such structures, their stability, the mode of motion of the ultimate particles, and the general energy relations involved in the dissociation and formation of lattices (cf. M. Born and Landé, *Ber. Deutsch. Phys. Ges.*, 1918 onwards; *Zeitsch. fur Physik*, 1920 onwards).

As shown by the X-ray method the significant units in crystal salt structures are the atoms. By a refinement of the method, Debye and Scherrer (*Physikal. Zeitsch.*, **19**, 474, 1918) have even shown that the electrons belonging to an atom are concentrated inside a very small space around the nucleus, the radius of the space being about one-tenth of δ_0 the lattice constant, this term denoting the distance between two similar atoms.

From Rubens' work on the residual rays characteristic of salt crystals it follows that the atoms carry an electrical charge; they are, in fact, ions. Born (*Sitzungsber. Preuss. Akad.*, 1918, p. 604), has shown the magnitude of the charge on each atom in the following way.

On the classical electro-magnetic theory of radiation we would expect to find $n^2 = D$, where n is the refractive index of the crystal lattice for infinitely long waves and D is the dielectric capacity. As is well known, for wave-lengths in the ultra-violet, visible, and short infra-red regions, n^2 is less than D . Over a wide range in the far infra-red region, Born points out that the refractive index n_r varies only very slightly with the wave-length, that is n_r in the case of diatomic crystals is independent of the molecular forces which give rise to anomalous dispersion and depends only upon the masses of and charges upon the atoms. Born has obtained an expression for the quantity $(D - n_r^2)$, which expression contains the product of the wave-length considered into the electric charge on the atom. The necessary data on the positions of the residual rays, the refractive indices, and the dielectric constants in the case of a number of crystals of different substances have been obtained by Rubens and from these it is thus possible to calculate the charge on the atoms. This is found to be identical, within the limit of error, with the charge on an electron.

The interpretation of the physical properties of the crystal lattice,

such as its compressibility, involve a knowledge of the laws of attraction and repulsion existing in the lattice. The purely electrostatic attraction between cations and anions in the lattice varies necessarily as the inverse square of the distance apart. To account for stability it is necessary also to postulate repulsions between the cations and anions. Born has found that this force varies as the inverse tenth power of the distance; that is, the potential of this force varies as the inverse ninth power of the distance. Born and Landé have shown that such a law accounts quantitatively for the compressibility of diatomic crystals. The principle of the method is as follows.

We begin with the self-evident expression for δ_0 , the lattice constant for the case of a regular crystal of the NaCl type, which has four similar charged atoms in each unit elementary cube—

$$\delta_0 = \sqrt[3]{\frac{4(m^+ + m^-)}{N\rho}} = 1.86 \times 10^{-8} \sqrt[3]{\frac{m^+ + m^-}{\rho}} \quad (1)$$

where m^+ and m^- are the masses of the ions, ρ the density of the crystal and N the Avogadro number.

We have next to consider the potential energy Φ of the elementary cube. This may be written—

$$\Phi = -\frac{a}{\delta} + \frac{b}{\delta^n} \quad (2)$$

in which the first term on the right hand side refers to the electrostatic attraction of the atomic charges regarded as points, the second to the repulsive force between the atoms due to the electrons concentrated around each nucleus. The equilibrium condition requires that Φ should be a minimum, that is,

$$\frac{d\Phi}{d\delta} = \frac{a}{\delta^2} - \frac{nb}{\delta^{n+1}} = 0 \quad (3)$$

For the equilibrium position, δ becomes δ_0 , a quantity the numerical value of which can be obtained from X-ray measurements or by means of equation (1). Regarding δ_0 as known we have the following expression for b —

$$b = \frac{a}{n} \delta_0^{n-1} \quad (4)$$

By further differentiation of (2) and taking (4) into account we can write the potential energy of the elementary cube in the form of a series:

$$\Phi = \Phi_0 + \frac{a(n-1)}{\delta_0^3} \cdot \frac{(\delta - \delta_0)^2}{2} + \text{etc.}$$

Writing the change in volume of the cube as Δ we have,

$$\Delta = \delta^3 - \delta_0^3 = 3\delta_0^2(\delta - \delta_0),$$

since in general δ is very nearly the same as δ_0 .

Whence

$$\Phi = \Phi_0 + \frac{a(n-1)\Delta^2}{18\delta_0^7}$$

Now, pressure, p , can be defined as the change of potential energy with the volume. That is—

$$p = - \frac{d\Phi}{d\Delta} = - \frac{a(n-1)\Delta}{9\delta_0^7}$$

Further, the compressibility κ of the crystal is given by :

$$\kappa = - \frac{1}{v} \frac{dv}{dp} = - \frac{1}{\delta_0^3} \frac{d\Delta}{dp} \quad (5)$$

whence

The calculation of a , as given by Born and Landé (*Sitzungsber. k. preuss. Akad.*, 1918, p. 1048), is—

$$a = 13.95 e^2 \quad (6)$$

where e is the electronic charge in electrostatic units, this value being of course independent of δ_0 . Setting $e = 4.774 \times 10^{-10}$, and combining equations (1), (5) and (6) we obtain—

$$n = 1 + 3.505 \times 10^{-13} \times \frac{1}{\kappa} \left(\frac{m^+ + m^-}{\rho} \right)^{4/3} \quad (7)$$

The expression allows us to calculate $(n+1)$ the exponent of the repulsive force. The values thus obtained for this quantity are given in the following table. The compressibility data are those of Richards and Jones (*J. Amer. Chem. Soc.*, **31**, 158, 1909):—

Salt	m^+	m^-	ρ	κ Observed ($\times 10^{12}$).	n (Calculated from Equation 7).
NaCl	23.0	35.5	2.17	4.1	7.91
NaBr	23.0	79.9	3.01	5.1	8.63
NaI	23.0	126.9	3.55	6.9	8.47
KCl	39.1	35.5	1.98	5.0	9.85
KBr	39.1	79.9	2.70	6.2	9.80
KI	39.1	126.9	3.07	8.6	9.33
TlCl	204	35.5	7.02	4.7	9.25
TlBr	204	79.9	7.54	5.1	9.67
TlI	204	126.9	7.06	6.7	9.84

The mean value of n is 9.20. If we assume that n is an even integer it follows that

$$n = 9.$$

That is, the repulsive force as calculated from the compressibility varies as the inverse *tenth* power of the distance between the ions.

In the case of calcium halides, which involve a divalent cation, the structure of the lattice differs from that of the salts referred to above, thereby giving rise to a different value for a . Frl. Bormann (*Zeitsch. Physik*, **1**, 55, 1920) calculates a for CaF_2 to be $46.93e^2$. Employing equation (5) and substituting the known value of the compressibility, it is found that n for this case is 7.20.

No compressibility data are available in connection with lithium salts. The behaviour of these salts may be expected to differ considerably from that of the other alkali halides because of the fact that the lithium ion possesses only two electrons and cannot therefore exhibit cubical symmetry. The exponent n should therefore be 5 instead of 9 (*cf.* Born, *Ber. Deutsch. phys. Ges.*, **21**, 14, 1919).

Note on the expression for p . The expression already employed is

$$p = - \frac{a(n-1)\Delta}{9\delta_0^7}.$$

This is an approximation, only two terms out of a series having been employed. This arises from writing the approximation $\Delta = 3\delta_0^2(\delta - \delta_0)$. The exact value for p is obtained by differentiating equation (2), which gives—

$$p = - \frac{a}{3\delta^4} \left(1 - \frac{\delta_0^{n-1}}{\delta^{n-1}} \right).$$

That these two expressions for p are approximately the same may be seen as follows—

As an approximation we can write,

$$\delta^{(n-1)} - \delta_0^{(n-1)} = (\delta - \delta_0)(n-1)\delta^{n-2}.$$

Hence, from the exact equation for p we obtain—

$$\begin{aligned} p &= - \frac{a(\delta - \delta_0)(n-1)\delta^{n-2}}{3\delta^4\delta^{n-1}} \\ &= - \frac{a(n-1)(\delta - \delta_0)}{3\delta^5} \\ &= - \frac{a(n-1) \cdot 3\delta_0^2(\delta - \delta_0)}{9\delta^5\delta_0^2} \\ &= - \frac{a(n-1)\Delta}{9\delta_0^7} \text{ approximately.} \end{aligned}$$

*The value assigned to n in the case of the alkali halides (other than that of lithium) is of great importance in connection with the structure of the atom in general. Thus Born and Landé (*Sitzungsber. Preuss. Akad.*, 1918, p. 1048, *Ber. Deutsch. phys. Ges.*, **20**, 292, 1918) have shown that the early Bohr model (later discarded by Bohr himself), when applied to crystals, permits of a calculation of the lattice constant δ_0 which is in reasonably good agreement with the "observed" value (*i.e.* that given by equation (1) *supra*), but at the same time gives rise to a force of repulsion between two oppositely charged atoms the potential of which varies as the inverse fifth power of the distance. This in turn leads to values for the compressibility of the crystal which are about double those observed. The discrepancy is sufficiently great, according

to Born, to make it necessary to substitute for Bohr's *early* model an alternative one. Born finds that the cubical atom model due to Lewis and Langmuir actually leads to the inverse ninth power relation for the potential of the repulsive force in agreement with the results obtained above for alkali halides.

Thus far we have dealt with the purely physical aspect of the lattice theory. Its importance becomes even greater when we turn to the chemical applications. We shall first consider the heat of dissociation of the crystal lattice (*cf.* Born, *Ber. Deutsch. phys. Ges.*, **21**, 13, 1919).

In the formation or dissociation of a crystalline substance the potential electrical energy Φ (equation (2) *supra*) of the lattice must manifest itself in the form of heat. The lattice theory can therefore be tested by comparing the calculated heat effect with that observed. By combining equations (2) and (4) we obtain the following convenient expression for the lattice energy—

$$\Phi = -$$

The term Φ refers to the normal state of the elementary cube which in the case of salts of the NaCl type contains four ions of each kind, that is four molecules in the ordinary chemical sense. If N is the Avogadro number per gram-molecule it follows that the lattice energy is $N\Phi/4$. This quantity may be denoted by $-U$, where U represents the work necessary to dissociate completely one gram-molecule of the crystal into free ions (not into atoms or molecules). Strictly U refers to absolute zero; its value will however be approximately the same at ordinary temperatures. We thus obtain the following important result on the basis of the lattice theory—

$$U = \frac{Na}{4\delta} \left(\frac{n-1}{n} \right) \quad (8)$$

Making use of equation (1) and substituting the numerical values for the constants and converting to kilocalories we obtain—
For lithium salts ($n = 5$),

$$U = 490 \sqrt[3]{\frac{\rho}{m^+ + m^-}}$$

For the remaining alkali salts ($n = 9$).

$$U = 545 \sqrt[3]{\frac{\rho}{m^+ + m^-}}$$

Values of U calculated by Born by means of these equations are quoted in the following table. The values in the case of the calcium salts have been calculated by Fr. Bormann (*loc. cit.*).

LATTICE ENERGY PER GRAM-MOLECULE (IN KILO-CALS.).

Salt.	U.	Salt.	U.
LiCl	179	LiI	153
NaCl	182	NaI	158
KCl	163	KI	144
RbCl	155	CaF ₂	612
CsCl	156	CaCl ₂	483
LiBr	167	CaBr ₂	454
NaBr	171	CaI ₂	424
KBr	155	TiCl	169

Landé showed later (*Zeitsch. Physik*, **2**, 396, 1920) that the value $n = 9$ employed by Born, in what would be regarded as the simplest form of the lattice theory, holds exactly only for two ions having the same number of electrons each. As regards the lattice energy U , somewhat different values have been calculated by Fajans and Herzfeld (*Zeitsch. Physik*, **2**, 309, 1920) by modifying Born's expression for the potential energy so as to take into account terms containing the inverse fifth and seventh powers of the distance as well as the ninth. "The theory removes the discrepancy in the relative magnitudes of the lattice energies of the respective sodium and potassium haloids and, moreover, explains the smaller relative value of the repulsion potential derived from available compressibility data in the case of the sodium salts as compared with the potassium salts."

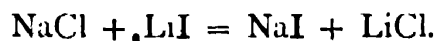
The Fajans-Herzfeld values for U are—

NaF . . .	210.4	NaBr . . .	159.7
KF . . .	192.2	KBr . . .	150.4
RbCl . . .	154.6	RbI . . .	135.8
NaCl . . .	170.0	NaI . . .	146.7
KCl . . .	159.0	KI . . .	139.1
RbBr . . .	146.5		

Fajans and Herzfeld have also calculated the values of the radii of the ions composing the alkali halide lattices. The following results were obtained :—

Ion.	Na ⁺	K ⁺	Rb ⁺	F ⁻	Cl ⁻	Br ⁻	I ⁻
Radius $\times 10^8$ in cm.	0.517	0.794	0.914	0.75	0.953	1.021	1.122

No direct evidence is available for testing the general accuracy of the individual values of U , since the observed heats of formation of salts from their elements involve the latter in the atomic or molecular form as distinct from the ionic form. A comparison is possible, however, by considering a type of reaction which entails only an exchange of ions in the crystal lattice, the reactants and resultants being in the solid state



The difference in energy ΔU between the initial and final states is given by—

$$\Delta U = U_{\text{NaCl}} + U_{\text{LiI}} - U_{\text{NaI}} - U_{\text{LiCl}} \quad (9)$$

The value of ΔU can be obtained from the data already given. Further, the heat of formation Q of each of these salts from their elements is known, *e.g.* $\text{NaCl} = \text{Na} + 1/2\text{Cl}_2 + Q_{\text{NaCl}}$ etc.

Whence the net heat effect ΔQ of the above reaction is given by—

$$\Delta Q = Q_{\text{NaCl}} + Q_{\text{LiI}} - Q_{\text{NaI}} - Q_{\text{LiCl}} \quad (10)$$

and, if the theory is correct, ΔU should be identical with ΔQ .

In the case of the above reaction ΔU lies between -2 and -3 whilst $\Delta Q = -4$. The sign and order of magnitude is correct, but the method obviously leaves much to be desired since the results to be compared represent small differences between very large quantities.

Born has attempted an alternative mode of comparison by taking into consideration the energy required to ionise the gaseous atoms from which the salts could be formed. Thus, the formation of crystalline NaCl from its elements could be analysed into the following stages:—

1. Vaporisation of metallic sodium into isolated atoms, and ionisation of the latter. The total energy required for this is denoted by Z_{Na} corresponding to the process: $\text{Na (solid)} \rightarrow \text{Na (gas)} \rightarrow \text{Na}^+ + \ominus$.

2. Dissociation of chlorine gas into its atoms and ionisation of the latter, the total energy required being Z_{Cl} , corresponding to $1/2 \text{ Cl}_2 \text{ gas} \rightarrow \text{Cl}^+ + \ominus$.

3. There is also a term apparently not taken into account by Born, namely, the energy evolved in the conversion of positively charged chlorine ion according to the scheme: $\text{Cl}^+ + 2\ominus \rightarrow \text{Cl}^-$ into the negatively charged form. This may be denoted by Z'_{Cl} . Adding the three stages together we obtain—

$$Q_{\text{NaCl}} = U_{\text{NaCl}} + Z'_{\text{Cl}} - Z_{\text{Na}} - Z_{\text{Cl}}.$$

Similarly for KCl—

$$Q_{\text{KCl}} = U_{\text{KCl}} + Z'_{\text{Cl}} - Z_{\text{K}} - Z_{\text{Cl}}.$$

Subtracting, we obtain—

$$Q_{\text{NaCl}} - Q_{\text{KCl}} = U_{\text{NaCl}} - U_{\text{KCl}} - Z_{\text{Na}} + Z_{\text{K}}$$

which may be rewritten thus—

$$Z_{\text{Na}} - Z_{\text{K}} = U_{\text{NaCl}} - U_{\text{KCl}} - Q_{\text{NaCl}} + Q_{\text{KCl}}.$$

The left hand side depends only upon the metals and not upon the halogens. We should therefore obtain the same value for $(Z_{\text{Na}} - Z_{\text{K}})$ or ΔZ from different halogen salts, provided the values of U which are based on the lattice theory are sufficiently correct. The following table contains the results obtained:—

ΔZ .	F.	Cl	Br.	I.	Mean.
$Z_{\text{Li}} - Z_{\text{K}}$	...	+ 28	+ 28	+ 28	+ 28
$Z_{\text{Na}} - Z_{\text{K}}$	+ 22	+ 27	+ 23	+ 25	+ 24

In so far as this mode of testing has value the conclusion arrived at above is borne out.

Born points out further that the Z term for any metal is made up of the latent heat of vaporisation, D , at absolute zero, together with the work, J , of ionising the gram atom, so that $Z = D + J$. From the known values of D and J it should be possible therefore to evaluate Z , and consequently ΔZ , for any pair of metals. The results could then be compared with the numbers such as those given in the final column of the preceding table. Unfortunately the values of D are known only very approximately and consequently it is almost impossible to apply the method. The results such as they are are favourable to the theory. On this basis Born is even able to find evidence in favour of $n = 5$ rather than $n = 9$ for the lithium salts.

A more exact test of the lattice theory as expressed in equation (8) has been carried out by Fajans (*Ber. Deutsch. Phys. Ges.*, **21**, 542, 1919) based on the heats of solution of salts. Let us take the case already considered namely: $\text{NaCl} + \text{LiI} = \text{NaI} + \text{LiCl}$.

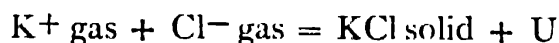
Sodium chloride and lithium iodide mixed together are dissolved in a given quantity of water and the heat effect observed. A similar measurement is carried out with a mixture of sodium iodide and lithium chloride, using the same amount of water. The difference between the two observed heat effects gives the quantity $\Delta(Q)$ which is identical with ΔU (equations (9) and (10)), for in both cases the resulting solutions are identical in composition. Instead of working with mixed salts the values for individual salts may be employed, provided the dilution is so large that the limiting heat value has been attained in each case. This condition has been realised in a number of cases in which the heat of solution has been determined. Making use of such data Fajans gives the following table in which ΔL , which stands for the value of $\Delta(Q)$ as determined by this method, is compared with ΔU obtained on the basis of the lattice theory. The symbol L stands in general for heat of solution.

Reaction	ΔU .	ΔL .
$\text{KCl} + \text{LiBr} = \text{KBr} + \text{LiCl}$	+ 4	3.6
$\text{KCl} + \text{LiI} = \text{KI} + \text{LiCl}$	+ 7	7.2
$\text{KCl} + \text{NaBr} = \text{KBr} + \text{NaCl}$	+ 3	2.0
$\text{KCl} + \text{NaI} = \text{KI} + \text{NaCl}$	+ 5	3.4
$2\text{KCl} + \text{CaBr}_2 = 2\text{KBr} + \text{CaCl}_2$	+ 9	8.5
$2\text{KCl} + \text{CaI}_2 = 2\text{KI} + \text{CaCl}_2$	+ 12	

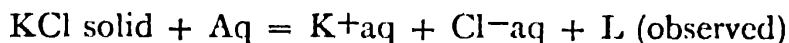
The agreement between ΔU and ΔL is satisfactory.

Fajans (*loc. cit.*, p. 549) has further investigated the individual heat of solution, L , of single salts, pointing out that this quantity is made up of two effects (*a*), the energy required to dissociate the salt into free gaseous ions ($-U$), and (*b*) the heat evolved when these ions are dissolved in water. If the solution be very dilute it follows that the

heat evolved in (b) must be an additive effect due to the anions and cations separately. This heat effect is regarded by Fajans as heat of "hydration" of the gaseous ions, the term hydration being taken to mean the condensation of an indefinite (non-stoichiometric) number of water molecules around the ion in a manner analogous to electrostriction. It must be emphasised that it is a gaseous ion which is involved in this; the values obtained for such heats of hydration bear no relation to the much smaller heat quantities usually attributed to the formation of definite stoichiometric hydrates of ions in solution. Taking the case of potassium chloride we can write—



where U is given by the lattice theory, and



whence, $\text{K}^+ \text{ gas} + \text{Cl}^- \text{ gas} + \text{Aq} = \text{K}^+ \text{aq} + \text{Cl}^- \text{aq} + U + L.$

From this it follows that W (cation + anion), the heat of hydration of both ions (originally gaseous) = U + L.

The following typical results illustrate the extremely high values obtained in this way. The heat effect is given in kilo-calories per gram-molecule.

Salt.	$W_{(\text{cation} + \text{anion})}$.	Salt.	$W_{(\text{cation} + \text{anion})}$
LiCl	187	CaCl ₂	428
NaCl	180.5	NaBr	171
KCl	159	KBr	150
RbCl	150	KI	139
CsCl	151	TlCl	159

The calculation just given affords values for the heat of hydration of both gaseous ions. Fajans proceeds next to calculate the heat of hydration of individual ions. It is necessary, in the first place, to consider the heat of formation of the ion in solution from the corresponding element. This quantity is determined by the electrochemical method of Ostwald (*Zeitsch. physikal. Chem.*, **11**, 506, 1893) and of Jahn (*Ibid.*, **18**, 421, 1895). The method involves the absolute value of the standard electrode and is therefore not very exact. In the case of hydrogen the formation of the ion in solution according to the scheme: $\text{H}_2 \text{ gas} - 2 \ominus + \text{aq} \rightarrow 2\text{H}^+ \text{aq}$, has a nett heat effect which is almost zero. In the analogous case of potassium the heat effect is 62 kilo-cals. per gram-atom approximately. We have next to carry out this process by another path, namely, by obtaining the value of the energy absorbed in vaporising an atom of the element and then in ionising this atom, the resulting ion being imagined to be dissolved in the solvent and becoming hydrated in this process. On proceeding in this manner and also allowing for the heat of vaporisation of the

electrons from the platinum in the case in which the hydrogen electrode is employed—a correction pointed out later by Born (*Zeitsch. Physik*, **1**, 45, 1920)—values were obtained for W , the heat of hydration of individual gaseous ions. These values expressed in kilo-calories per gram ion are given in the following table:—

Cations	Heat of Hydration	Anions	Heat of Hydration
H ⁺	262	Cl ⁻	77
Li ⁺	110	Br ⁻	68
Na ⁺	103	F ⁻	57
K ⁺	82	—	—
Rb ⁺	73	—	—
Cs ⁺	74	—	—
Tl ⁺	82	—	—
Ca ⁺⁺	344		

Taking the values of W quoted as substantially correct Born has shown that a simple mode of calculation of the heat of hydration of gaseous ions presents itself. The expression involves the radius of the ion and this can be calculated by employing the above heat values. The results are of the correct order of magnitude. Briefly Born's method is as follows:—

Consider a spherical positive or negative ion of radius r , carrying the charge Ze , where Z is the valency. The electrical field E *outside* the sphere when the latter is placed in a medium of dielectric capacity ϵ possesses the energy—

$$U = \frac{1}{8\pi\epsilon} \int E^2 dS$$

where the integration has to be carried out over the whole volume outside the sphere

$$E = Ze/r^2, \text{ and } dS = r^2 dr d\Omega$$

in polar co-ordinates, where $d\Omega$ is an element of the unit spherical volume.

Hence

$$U = \frac{1}{8\pi\epsilon} \cdot 4\pi \int_0^\infty \frac{Z^2 e^2}{r^4} r^2 dr = \frac{Z^2 e^2}{2\epsilon r}$$

The electro-static energy of the ion is therefore

$$\begin{array}{ll} \text{in air } (\epsilon = 1) & : \quad Z^2 e^2 / 2r, \\ \text{in water } (\epsilon = 81) & \quad Z^2 e^2 \end{array}$$

The work obtained by bringing the ion into the water is the difference of the two energy quantities. Considering one gram ion and converting into kilo-cals., the heat of hydration is given by

$$1.64 \cdot 10^{-6} Z^2 / r.$$

Employing the values already obtained for W , Born calculates r_i and compares it with r_a , the radius of the atom as obtained from the density and the ordinary atomic volume of the solid element. The values are given in the following table:—

Element.	$r_i \times 10^8$.	$r_a \times 10^8$	Element.	$r_i \times 10^8$.	$r_a \times 10^8$
H	0.625	1.68	Tl	2.0	1.89
Li	1.49	1.72	Ca	1.91	2.16
Na	1.59	2.10	Cl	2.13	1.94
K	2.0	2.62	Br	2.41	2.09
Rb	2.24	2.81	I	2.88	2.16
Cs	2.22	3.02	—	—	—

It is evident that r_i is of the correct order of magnitude which, in so far as this goes, supports the simple theory outlined. It is noteworthy that in the case of Ca the value of r_i is obtained by setting $Z = 2$ (since the ion is divalent); discordant results would be obtained on any other value of Z . For all positive ions, with the exception of Tl, $r_a > r_i$; for negative ions $r_i > r_a$. From this Born argues that in the formation of a positive ion the outermost electrons are torn from the atom, whilst electrons are added in the case of the negative ions.

The Affinity of Neutral Halogen Atoms for Electrons.¹

The affinity of a neutral atom for an electron is measured by E , where E is defined as the work which must be expended to remove an electron from a (negatively charged) halogen *ion*. Born shows that E is a positive quantity, that is, the neutral halogen atom has a positive affinity for an electron. Born's argument is as follows. We begin with solid potassium chloride and imagine it decomposed into free gaseous ions in two different ways.

The first way corresponds to the direct dissociation (ionisation) which involves an absorption of U energy units, namely, 163 kilo-cals. per gram-molecule.

The second way corresponds to the decomposition of the salt into its electrically neutral elements, namely, metallic potassium and gaseous molecular chlorine, whereby Q units of heat are absorbed, *viz.* 106 kilo-cals. per gram-molecule of KCl. The potassium is then vaporised, the heat absorbed being about 21 kilo-cals., and the atoms are ionised into ions and free electrons. The latter process corresponds to the ionisation potential of the metallic vapour which is equivalent to 99 kilo-cals. per gram-atom in the case of potassium. At the same time the molecular chlorine is dissociated into its atoms, the heat absorbed being taken by Born to be 53 kilo-cals. per gram-atom (although this is probably too

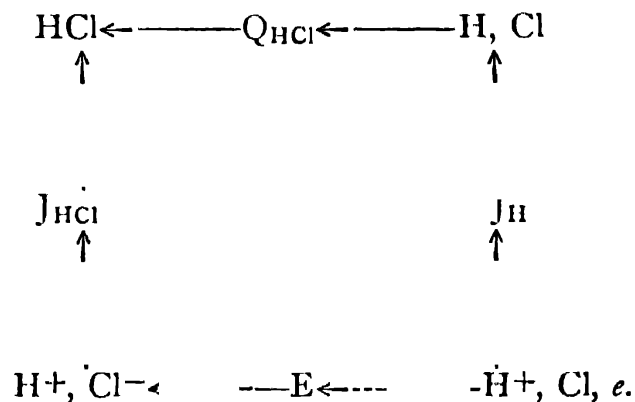
¹ Born, *Ber. Deutsch. phys. Ges.*, **21**, 679, 1919; Fajans, *ibid.*, 714; Foote and Mohler, *Journ. Amer. Chem. Soc.*, **42**, 1832, 1920.

high a value), and each of these atoms attaches itself to one of the electrons set free by the ionisation of the potassium vapour.

We have thus arrived at the same end point by two different paths. Equating the energy terms, it is found that the union of an electron with the chlorine, bromine and iodine atom respectively, involves the evolution of 116, 87, and 81 kilo-cals. per gram-atom.

It is important to observe that whilst the affinity between a halogen atom and a free electron is thus found to be a positive quantity, the reverse is true of the hydrogen atom, according to the ingenious calculation of Klemenc (*Zeitsch. Elektrochem.*, **27**, 470, 1921). Klemenc finds that energy in amount 39.4 kilo-cals. has to be *absorbed* in order to render possible the process: $\text{H} + \ominus \rightarrow \text{H}^-$.

Returning to the case of the halogens, it must be pointed out that at present we have no means of verifying the values quoted in a direct manner. Born has, however, tested the general accuracy of the calculated value by an indirect method, based on the ionisation of the hydrogen haloids. The mode of ionisation in this case was assumed by Born to be: $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$, and this assumption was later confirmed experimentally by Foote and Mohler (*loc. cit.*). The corresponding energy term we shall denote by J_{HCl} . The various inter-relationships in the case of *gaseous* hydrogen chloride are shown conveniently by the following scheme, which is due to Haber (*Ber. Deutsch. phys. Ges.*, **21**, 754, 1919):—



Symbols separated by commas indicate free atoms or ions which are supposed to be at an infinite distance from one another. The direction of the arrows corresponds to an evolution of energy. The quantity J_{HCl} differs from U_{HCl} by an amount identical with the heat of sublimation of solid hydrogen chloride. Q_{HCl} denotes the heat which would be evolved by the union of atomic hydrogen with atomic chlorine, a quantity which is known to be 117 kilo-cals. per gram-molecule of HCl formed. J_{H} denotes the energy of ionisation of a free hydrogen atom, namely, 310 kilo-cals. corresponding to the ionisation potential 13.4 volts. The symbol e stands for an electron. Passing from the right-hand lower corner of the diagram to the upper left-hand corner by the two paths and equating the energy terms, it is found that $J_{\text{HCl}} = 311$ kilo-cals., this quantity being based in part on the value of E for chlorine calculated

by the lattice theory. The quantity, 311 kilo-cals. corresponds to an ionisation potential of 13.5 volts. Foote and Mohler (*loc. cit.*) have found by direct experiment 14 volts, which corresponds actually to 320 kilo-cals. The agreement is satisfactory. Born finds that the value of J for HBr and HI are very similar to that for HCl, the values being

$$\begin{aligned} J_{\text{HCl}} &= 320 \text{ (311) kilocal.} \\ \bullet \quad J_{\text{HBr}} &= 311 \quad \quad \quad \text{,,} \\ \bullet \quad J_{\text{HI}} &= 302 \quad \quad \quad \text{,,} \end{aligned}$$

Born and Frl. Bormann (*Zeitsch. Physik*, **1**, 250, 1920) have also calculated $J_{\text{H}_2\text{S}}$ to be 716 kilo-cals., whilst Landé (*ibid.*, p. 400) calculates J_{HF} to be 350 kilo-cals., and $J_{\text{H}_2\text{O}}$ 533 kilo-cals. corresponding to the process: $\text{H}_2\text{O (gas)} \rightarrow \text{O}^- + \text{H}^+ + \text{H}^+$.

The energy of ionisation, J, of the hydrogen haloids, has also been calculated by Knipping (*Zeitsch. Physik*, **7**, 328, 1921) who gives the following values:—

Gaseous Haloid	J in Kilo-Cal.	Ionisation Potential
HCl	331	14.4 volts
HBr	317	13.8 "
HI	308	13.4 "
HCN	357	15.5 "

The quantity, J, for hydrogen haloids has been analysed by Haber (*loc. cit.*) who has shown that it can be accounted for on the basis of a displacement of the nucleus of the halogen ion with respect to its electrons when the nucleus is attached to a hydrogen nucleus to form the hydrogen haloid. The normal arrangement for a halogen ion is represented by a cube with the nucleus at the centre and the electrons at the corners. This is the form in the alkali chlorides, for example; in hydrogen chloride the halogen ion is deformed.

It may be mentioned that Cuthbertson's value for the dispersional frequency of hydrogen chloride corresponds to the wave-length 918.67 Å.

Converting this into frequencies and applying the principle of the photo-chemical equivalent, we find that $Nh\nu = 309$ kilo-cals., where N is the number of molecules in one gram-molecule and ν is the dispersional frequency. This energy value is in satisfactory agreement with that obtained above.

It is noteworthy that the energy of ionisation of gaseous hydrogen chloride (into two oppositely charged ions) is almost the same in magnitude as the energy of ionisation of a free hydrogen atom into a hydrogen nucleus and an electron. This means that the affinity of the hydrogen nucleus for an electron is practically the same as the affinity of the hydrogen nucleus for a halogen ion. This is considered in some detail by Haber (*loc. cit.*), who concludes that the heat of formation of all the alkali chlorides in the gaseous state from the gaseous atomic elements is the same as that for hydrogen chloride, namely, 117 kilo-cals. per gram-molecule of salt. In the course of his considerations Haber estimates that the heat of sublimation of the alkali haloids is of

the order 60 kilo-cals., a very large quantity when compared with the corresponding term for the solid hydrogen haloids, namely, 4 to 5 kilo-cals. per gram-molecule. Haber shows, however, that the above value for the heat of sublimation of the salts is in agreement with their high sublimation temperature. Further, the heat of sublimation of the alkali chlorides has been calculated to be about 50 kilo-cals. by Reis (*Zeitsch. Physik*, **1**, 294, 1920; cf. also Weinberg, *ibid.*, **3**, 337, 1920).

For this purpose Reis assumes that the ionisation of the gaseous molecule of the salt can be treated similarly to the ionisation of the molecule in the crystalline state if allowance be made for the fact that, in the solid, each pair of ions is surrounded by other ions, whilst in the gaseous state the pair of ions is isolated and consequently their mutual attraction is increased. The difference between the two energies of ionisation necessarily gives the heat of sublimation. The following are representative values obtained in this way. The quantities are given in kilo-cals. per gram-molecule:—

	NaCl.		NaI.	KCl.		KI.	RbCl.	CsCl.
Heat of sublimation :	58	55	51	52	50	46	50	50

Weinberg's values are approximately 5 kilo-cals. less.

Haber has applied quantum considerations, in the form of the law of the photochemical equivalent, to the alkali haloid (ionic) crystal lattice in the following manner. The dispersional frequency ν_0 of the solid salt (obtained from measurements of the refractive index) is regarded as representing the most violent electronic movement of which the lattice is capable, and therefore corresponding probably to the energy U required for its ionisation. On this basis we write: $U = N h \nu_0$, where N is the Avogadro constant. In the case of potassium chloride (sylvine) the limiting wave-length, which corresponds with ν_0 , has been found to be $160.7 \mu\mu$, that for rock salt being $156.3 \mu\mu$. Hence $N h \nu_0$ for KCl and for NaCl is calculated to be 177 and 182 kilo-cals. per gram-molecule respectively, whilst U as calculated by Born is 163 and 182 kilo-cals. respectively. The agreement is surprisingly good in view of the somewhat uncertain nature of the theoretical basis employed by Haber. In the case of other salts for which Born has calculated U the necessary refractive index measurements have not yet been made. Haber, however, makes use of his "square-root rule," already mentioned in Chapter VI., which connects the known characteristic infra-red vibration frequency ν_r of the salt, as determined by Rubens, with the quantity ν_0 . Haber's formula is—

$$\nu_0 = \nu_r \times 42.81 \sqrt{\frac{4m_1m_2}{m_1 + m_2}}$$

where m_1 and m_2 are the atomic weights of the elements composing the salt. On this basis the following values of $N h \nu_0$ have been calculated in kilo-cals. :—

Salt	NaCl	KCl	KBr	KI	HCl	TlBr	TlI	LiF
$Nh\nu_0$	173	165	151	141	144	157	142	336
U Born	182	163	155	144	169	163	151	231

With the exception of lithium fluoride, where the discrepancy is very great, the degree of agreement is satisfactory.

We have now to consider *the structure of metals*. At first sight this might appear to be a simpler case than that of salts (in which at least two different kinds of atoms are present); actually, however, our knowledge of the structure of metals appears to be of a somewhat more speculative character than is the case with salts, at least salts of the simple alkali haloid type.

Metals are characterised by their electrical and thermal conducting capacity, properties which were formerly explained on the basis of freely moving electrons, each electron possessing considerable thermal capacity, since a freely moving electron should have at least the energy $(3/2)kT$ in virtue of translation. Determinations of the specific heats of metals, carried out to test the applicability of the quantum theory to heat content, have shown, however, that the heat capacity of electrons must be negligible, until extremely high temperatures are reached. The free electron theory consequently breaks down. In its place Lindemann (*Phil. Mag.* [vi.], **29**, 127, 1915) has suggested that a metal consists of two interleaved space lattices, one consisting of metallic ions, the other of electrons. On this basis, the electrical conductivity is due to the movement of the electron lattice as a whole through the ionic lattice. The resistance which the electron lattice experiences is due to the vibrations of the ions of the ionic lattice, which impede the movement of the electron lattice as a result of electrical repulsions. At very low temperatures, however, the vibrations of the ions are small and the electrical conductivity should be abnormally great. This corresponds with the known supra-conductive state discovered by Onnes at the temperature range below 3° absolute. If the metal is not pure the ionic lattice is heterogeneous, and the electron lattice has greater difficulty in moving through it. That is, the presence of an impurity should increase the resistance of a metal, a conclusion which is borne out by experiment. As the electron lattice moves through the ionic lattice at temperatures above zero it will transfer to the latter a certain amount of the kinetic energy which it has gained from the impressed electric field; in other words, the temperature of the metal will rise as a consequence of the passage of current. Lindemann shows that this theory of the metallic state is in agreement with Ohm's law. As regards thermal conductivity, on the lattice theory, heat is transmitted as elastic waves. The thermal conductivity of a metal may be regarded as the sum of the conductivities of the two lattices. The thermal conductivity of the ionic lattice is necessarily of the same order as that

of a salt crystal and is therefore negligible at ordinary temperatures. The conductivity of the electron lattice, on the other hand, will be large, for, as Lindemann shows, it will behave like an ionic lattice at a very low temperature where such lattices are known to possess high thermal conductivity. Further, the specific heat of the electron lattice, owing to its high limiting frequency, is extremely small. Thus, without attributing any measurable heat capacity to the electrons, it is possible to have a large thermal conductivity as a whole in the case of a metal. This is in excellent agreement with the results obtained from measurements of specific heats, and constitutes the main advantage of the electron lattice theory, as distinct from the older free electron theory. Lindemann has attempted to show further that the lattice theory is capable of explaining the magnitude of the photo-electric effect, even accounting for the difficulty that the energy of the photo-electron is sometimes greater than the incident energy of the light falling on one electron. On the lattice theory, a large part of the wave-front can act on the electron lattice, setting up an elastic wave sufficiently intense to eject an electron from the lattice.

A lattice theory of metals has also been worked out by Haber (*Sitzungsber. Preuss. Akad.*, 506, 990, 1919) based directly on Born's concepts. Haber finds that the metallic lattice energy U is of quite the same order of magnitude as that of haloid salts. Haber finds, however, that in the case of the alkali metals the exponent n in the potential of the repulsive force is very low, namely, between 2 and 4, in place of the average value 9 found for salts. This raises a very serious difficulty, since Born has shown that with a low value of n the electrons would not form a lattice. Borelius (*Phil. Mag.*, 40, 746, 1920) has shown, however, that employing a space lattice of the type actually given by X-ray measurements, the resulting average value for n , as determined from compressibility, is 9. Borelius concludes that in metals a symmetry other than that of the cube is indicated. It must be emphasised that Borelius assumes the electron lattice to be "fluid" and that only at very low temperatures does it "solidify" in the sense of Lindemann.

The Molecular Lattice.

We return once more to a consideration of the hydrogen haloids. It will be recalled that in the consideration of these compounds, *e.g.* hydrogen chloride, the substance was regarded as existing in the gaseous state and the quantity $J_{\text{HCl}} = 320$ kilo-cals. referred to the energy of ionisation of a gaseous mole of HCl. Reis (*loc. cit.*) has put forward certain important considerations in connection with the nature of the *lattice of crystalline hydrogen haloids*.

Reis points out the low heat of sublimation of hydrogen haloids as compared with that of the alkali haloids, and also the extremely high energy of ionisation (320 kilo-cals.), which is about twice as great as that of the alkali haloids (150-180 kilo-cals.). He also points out the relatively large molecular volume of the solid hydrogen haloids, and

finally concludes that the lattice in these cases must be very different from the lattice in the case of salts. This difference he attributes, very reasonably, to the existence of molecules as distinct from ions as the significant material units composing the lattice in the case of the solid hydrogen haloids. On this basis it follows that there are two lattice spacings, one "short," the other "long". The long one is the true analogue of the lattice constant δ already met with in the ionic lattice. The short spacing is the distance between the hydrogen nucleus and haloid nucleus in one and the same molecule. When vaporisation occurs the molecule as a whole leaves the solid and, since the attractions between molecules must be much less than that between ions, the latent heat of vaporisation is small compared with its value in the case of a true ionic lattice. Naturally a similar molecular lattice is to be expected in the case of organic compounds in agreement with the recent work on crystal structure by the X-ray method.

The molecular structure attributed to the lattice of the hydrogen haloids involves great deformation of the halogen ion (*vide* Haber, *supra*). These ions can no longer be cubical as they are in the case of alkali haloids. In the stable position the hydrogen nucleus approaches the halogen nucleus very much more closely than is the case say with potassium and halogen nuclei, for in the latter case the atmosphere of electrons around each nucleus tends to keep them apart. Finally, evidence for the disposition of the nuclei in the molecule of HCl is obtainable from a consideration of the electric moment of the molecule, that is, the product of the ionic charge into half the distance between the nuclei. From the dielectric property of HCl it follows that its electric moment is considerably less than that of the water molecule. Since the latter has the approximate value 2×10^{-18} (*cf.* Jona (*Physikal. Zeitsch.*, **20**, 18, 1919)) it follows that the electric moment for the hydrogen-haloid molecule is less than 10^{-18} . But if the radius of the molecule be given the not improbable value of 1×10^{-8} cm. the electric moment should be greater than 4×10^{-18} . The discrepancy here referred to is attributed by Reis to an effect due to the deformation of the halogen ion. This is probably true although the explanation is scarcely adequate.

Atomic and Molecular Magnetic Forces.

In the foregoing section an account has been given of the crystalline state from the point of view of electrostatics. It is now necessary to review briefly crystalline compounds from the point of view of electromagnetic forces.

That two electrons rotating in a certain manner with respect to one another will attract or repel electromagnetically with a force varying more rapidly than the inverse square of the distance has long been known. On the basis of the idea of electrons rotating in localised orbits which are small compared with the dimensions of the molecule, Oxley (*Phil. Trans.*, **214 A**, 109, 1914; **215 A**, 79, 1915; **220 A**, 247, 1920)

has investigated the problem of the extent to which the resulting electromagnetic forces may enter into and define the behaviour of crystalline substances. It is not suggested that electromagnetic considerations should replace electrostatic in general, but that rather the effects are superimposed. In certain cases the magnetic may predominate. Oxley's investigations are concerned mainly with the case of diamagnetic organic substances. The principal contribution consists in the demonstration that the local molecular field in a diamagnetic substance is comparable in magnitude with the ferromagnetic molecular field, being of the order 10^7 gauss. That this is a field of extremely high intensity is evident when we recall that the most intense field which can be produced artificially is of the order $10^4 - 10^5$ gauss. The principal experimental evidence advanced by Oxley is the change in the specific diamagnetic susceptibility (measured in the case of about 50 substances) which accompanies the change from the liquid to the solid state.

On Langevin's theory of magnetism, the molecule of a diamagnetic substance contains oppositely spinning systems of electrons, which counterbalance one another externally, so that the molecule as a whole possesses no initial magnetic moment. When an external magnetic field is applied, the frequency of rotation of one electronic system is increased, whilst the other is diminished, and the molecule becomes slightly polarised and distorted. This small differential effect accounts for the well-known Zeeman effect, and is also the origin of the small magnetic moment possessed by a diamagnetic substance when subjected to a magnetic field. The act of crystallisation can also be regarded as bringing about a similar distortion of the molecule, so that the difference in susceptibility of the solid and liquid forms may be employed to determine the order of magnitude of the local field of magnetic molecular force which is here assumed to give rise to the rigidity characteristic of the crystalline form.

Let us suppose that ΔM is the change in the moment, M , of an electron orbit produced by applying a magnetic field, H , τ being the period of rotation of the electron (of the order 10^{-16} sec.) and e/m the ratio of the charge to the mass of an electron. Langevin has shown that—

$$\frac{\Delta M}{M} = - \frac{H\tau e}{4\pi m} = 10^{-9} \cdot H.$$

If, as a result of crystallisation, the molecular field produced is of the order 10^7 gauss, then the value of ΔM is 10^{-2} , which would mean a change of 1 per cent. in the susceptibility. This is the order of the change observed in the case of aromatic compounds. Other evidence confirming the extremely high value ascribed to the molecular field is furnished by the results obtained with double refraction, magnetostriction, and magneto-rotation. Thus, when a liquid is brought into a magnetic field, it becomes slightly doubly refracting, and at the same time undergoes a small diminution in volume. Oxley shows that if a

field of 10^7 gauss could be applied (this being the field which is supposed to be produced by crystallisation), a double refraction comparable with that exhibited by quartz would be produced. Under the same field, the decrease in volume would be about 10 per cent., a value in good agreement with the observed change in volume on crystallisation in numerous cases.

It must be emphasised that, on the view expressed above, the molecule of a diamagnetic substance is locally ferro-magnetic, that is, one part of the molecule is a north-seeking, the other part a south-seeking, pole; this is regarded as the origin of molecular union. The repulsion observed when a diamagnetic substance is placed in a magnetic field is looked upon as purely an induction effect produced in a system of molecules, each of which has initially a zero magnetic moment.

Having considered the intensity, H_c , of the local molecular field, we have now to consider its energy. Let I denote the aggregate local intensity of magnetisation for all the molecules, n , in unit volume. Then $I = ni$, where i is the local magnetic moment of a single molecule. The potential energy E of 1 gram of the substance, in virtue of the grouping and distortion of the molecules constituting the crystalline form (that is, over and above the energy associated with 1 gram of the liquid) is then given by: $E = H_c I / 2\rho$, where ρ is the density of the crystal. If we assume that H_c is proportional to I , we can write $H_c = a'_c I$, where a'_c is a constant which Oxley shows is the reciprocal of the limiting local susceptibility of the crystalline medium under a field strength identical with that possessed by the molecular field itself. The energy E can therefore be written as $a'_c I^2 / 2\rho$, which is analogous to the expression $NI^2 / 2\rho$ obtained by Weiss for ferro-magnetic substances. The constant a'_c corresponds with N , both having the same physical significance for the respective kind of substance. Oxley shows that the numerical values of a'_c and N are comparable, as are also the I terms, so that the energy of the molecular field in the case of a diamagnetic, crystalline substance is of the same order of magnitude as that of a ferro-magnetic solid, namely, 10^9 ergs per gram. Now in the act of fusion the crystalline form is destroyed; the latent heat of fusion should therefore be of the order $10^9 / 4.2 \times 10^7$, or 25 cal. per gram. The following are a few experimental values—

Benzene	. 30 cals.	Chlorobenzene	. 30 cals.	Aniline	. 21 cals.
Nitrobenzene	. 22 „	Naphthalene	. 35 „	Pyridine	. 22 „

Reference must also be made to the variation in the specific heat of a crystalline solid as the melting temperature is approached. "In the crystalline state we must regard the molecules as orientated into definite positions with respect to their neighbours by these large inter-molecular forces. If at the higher temperatures the molecules undergo rotational vibrations about their mean positions, then it would be expected that the value of I^2 would be somewhat lessened by these vibrations, and we should therefore expect that a small fraction of the

energy associated with the grouping would be dissipated as the temperature is raised towards the fusion point. The effect this would have on the variation of the specific heat with temperature would be to add to the normal variation (expressed by Debye's theory) the following positive term—

$$\frac{\alpha'_c}{2\rho J} \cdot I \cdot \frac{\delta I}{\delta T}$$

where T is the absolute temperature and J the mechanical equivalent of the calorie." Nernst and Lindemann have found that close to the melting point there is an abnormal increase in the specific heat of diamagnetic substances, and in order to account for this on the above basis it is necessary to give to I a large value, such as that required by previous considerations. It is necessary to point out that only a small fraction of the energy term E will be dissipated below the fusion point, the major part of it being involved in the act of fusion itself.

Again, the frequency ν of the rotating electrons is given by—

$$\nu = He/2\pi m.$$

If the value ascribed to H be of the order 10^7 gauss, then ν is of the right order of magnitude for an optical frequency. If inside a molecule the intensity were 10^9 gauss, frequencies corresponding with X-rays would be accounted for.

Finally, the intermolecular magnetic field will determine from the point of view considered the tensile strength of the crystal, and, as the stresses will be different in general in different directions, planes of cleavage will occur. In this connection it is important to recall the experiments of Tyndall, who found that the cleavages of diamagnetic substances when placed in a magnetic field stand equatorial, whilst the cleavages of magnetic substances stand axial. Oxley finds in this further evidence that the forces which produce crystallisation are magnetic in nature.

"In any case it is clear that the magnetic forces cannot be ignored even when the electrostatic forces do predominate, and the complete theory has yet to appear which shall give to these two types of force the relative prominence which the experimental data demand."

CHAPTER IX.

(Systems in chemical equilibrium)—Relation between Nernst's heat theorem and the quantum theory—Mass action equilibrium and heat of reaction in terms of the quantum theory.

NERNST'S HEAT THEOREM AND THE QUANTUM THEORY.

WE have already seen (Chap. III.) that the quantum theory applied to atomic heat of solids leads us to expect that at very low temperatures the atomic heat will become practically zero. If we think of two solids A and B we can state that at low temperatures—

$$dU_A/dT = dU_B/dT = 0$$

or

$$d(U_A - U_B)/dT = 0.$$

If the solid substances A and B are the reactant and resultant respectively of a chemical reaction, the expression $(U_A - U_B)$ represents the change in internal energy, U accompanying the reaction. Hence the quantum theory leads to the conclusion that in a chemical reaction between solids at very low temperatures—

$$dU/dT = 0.$$

This, as far as it goes, is in complete agreement with Nernst's heat theorem which states (*cf.* Chap. XIII., Vol. II.) that—

$$\text{limit, } T = 0 \left\{ \begin{array}{l} dA/dT = 0 \\ dU/dT = 0. \end{array} \right.$$

To show that the relation $dA/dT = 0$ is likewise in agreement with the Planck-Einstein hypothesis regarding the energy distribution in solids, we may proceed as follows: As the molecules or atoms of a solid at very low temperatures do not possess any sensible kinetic energy of vibration, their mutual distance apart will change very little with temperature over a limited range in this region. Consequently, the mutual potential energy of the atoms or molecules will remain practically unchanged, and hence their free or available energy, which depends upon the potential energy, will also remain unchanged. That is, in the limit, when $T = 0$, $dA/dT = 0$. The same conclusion may be arrived at in a slightly different way. We know that the intensity of radiation, and therefore the amplitude of the resonators (*i.e.* the atoms), increases with the temperature according to a power law considerably greater than the first. Hence, as temperature falls the amplitude will decrease much more rapidly, finally becoming exceedingly small. Again, the potential

energy, and therefore the free energy, may be regarded as sensibly independent of the temperature when the temperature is low. It cannot be said, of course, that the validity of the Planck-Einstein theory is a proof of the validity of Nernst's heat theorem. They are, however, in agreement. This point will perhaps be rendered clearer by the following considerations.

We know that in the case of any process carried out reversibly, the Gibbs-Helmholtz equation states—

$$A - U = T \cdot (dA/dT),$$

Further, $A - U = Q$ where Q is heat absorbed in the process.

Hence $Q/T = S = (dA/dT)_m$ where S is the change in entropy of the system as a result of the process. Applying Nernst's theorem we conclude that at very low temperatures the change in entropy due to the process is zero. In other words, Nernst's theorem is identical with the statement that at absolute zero the entropy of all substances is the same. Planck has already pointed out (*cf* Chap. I.) that the quantum hypothesis is equivalent to the assumption that the entropy of all substances at absolute zero is zero also. This is really a special case of the conclusion involved in Nernst's heat theorem. The theorem and the quantum theory are therefore in agreement, but the heat theorem is independent of the quantum hypothesis.¹

Calculation of the Affinity of a Chemical Process from Thermal Data by the Simultaneous Application of Nernst's Heat Theorem and the Quantum Theory of Atomic Heats.

Equations (3) and (4) of Chap. XIII. of Vol. II., which express the Nernst heat theorem, contain certain coefficients β , γ , etc., which are calculated from measurements of the molecular or atomic heats of the reactants and resultants of the reaction considered. In principle, the introduction of the quantum theory (say in the form of the Nernst-Lindemann equation) is simply a matter of substitution of this equation in the original equations of Nernst for A and U . To indicate how this is carried out in practice it is necessary to put the Nernst equations into a more general form than that expressed by the equations (3) and (4) referred to.

The change, U , in the internal energy of a system as a result of a chemical reaction is, by definition, the difference of the internal energies of reactants and resultants, reckoned in terms of the stoichiometrical quantities required for the reaction. For any single substance Z we can write: $dU_z/dT = c_z$, where c_z denotes the molecular heat of the substance Z at constant volume.

Hence $U_z = \text{constant} + \int_0^T c_z dT$. Hence

¹ The relation between the heat theorem and the quantum theory is further considered by O. Sackur (*Annalen der Physik*, **34**, 455, 1911).

for the quantity U , which involves the algebraic sum of a number of such terms, we can write—

$$U = U_0 + \int_0^T \Sigma n c dT,$$

where U_0 is the change in internal energy accompanying the reaction at absolute zero, and n denotes the number of moles of reactants and resultants (with proper sign) which take part in the reaction.

We have now to express the molecular or atomic heat c of each reacting substance in terms of the Nernst-Lindemann equation. Having done this we find that the above integral may be evaluated thus—

$$\int_0^T \Sigma n c dT = \frac{3}{2} R \Sigma n \left(\frac{\beta_0 \nu}{e^{\beta_0 \nu / T} - 1} - \frac{\beta_0 \nu / 2}{e^{\beta_0 \nu / 2T} - 1} \right)$$

Hence—

$$U = U_0 + \frac{3}{2} R \Sigma n \left(\frac{\beta_0 \nu}{e^{\beta_0 \nu / T} - 1} + \frac{\beta_0 \nu / 2}{e^{\beta_0 \nu / 2T} - 1} \right) + \frac{3}{2} \Sigma n a T^{5/2} \quad (1)$$

The final term is an empirical correction, which has to be added to allow for the fact that the experimental measurements of molecular or atomic heats refer to constant pressure, whilst the quantities to which the Nernst-Lindemann expression refer are molecular or atomic heats at constant volume. Cf. Magnus and Lindemann (*Zeitsch. Elektrochem.*, **16**, 369 (1910)); a more exact correction is given by Nernst and Lindemann (*Zeitsch. Elektrochem.*, **17**, 817 (1911)).

We have now to consider the free energy term A . On the basis of the first and second laws of thermodynamics we have already seen that—

$$\frac{A}{T} = a - \int \frac{U}{T^2} \cdot dT.$$

Further, Nernst's theorem leads to the conclusion that $a = 0$ and therefore we can write—

$$A = - T \int \frac{U}{T^2} \cdot dT.$$

Again writing—

$$U = U_0 + \int_0^T \Sigma n c dT,$$

and substituting this in the above integral, and also substituting the Nernst-Lindemann expression, we obtain—

$$A = U_0 - \frac{3}{2} R \Sigma n \beta_0 \nu + \frac{3}{2} R T \Sigma n \left[\log_e (e^{\beta_0 \nu / T} - 1) + \log_e (e^{\beta_0 \nu / 2T} - 1) \right] - \frac{3}{15} \Sigma n a T^{5/2}. \quad (2)$$

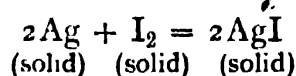
(Naturally the symbol a which occurs in the final correction term of equations (1) and (2) is quite distinct from the integration constant referred to above.)

Equations (1) and (2) express the Nernst heat theorem in terms of the quantum theory.

[NOTE.—The mode of obtaining equations (1) and (2) is given in detail in Pollitzer's article, *Die Berechnung chemischer Affinitäten nach dem Nernst'schen Theorem*, Ahrens Sammlung, 17, 1912. To facilitate calculation Pollitzer has included as an appendix a number of tables giving the Einstein and Nernst-Lindemann functions for various values of β_0 and ν .]

We now proceed to consider an actual case, namely, the affinity of silver for iodine investigated by U. Fischer (*Zeitsch. Elektrochem.*, 18, 283, 1912). The treatment of a number of difficulties met with is instructive and is therefore given in some detail.

The first question taken up by Fischer is the *heat of the reaction*—



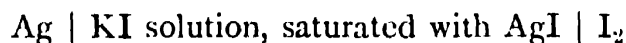
The direct measurements of Thomsen and of Berthelot being unsatisfactory, recourse was had to the Gibbs-Helmholtz equation—

$$A' - U = T \frac{\partial A'}{\partial T}$$

or

$$E - U = T \frac{\partial E}{\partial T}$$

as applied to the measurement of the E.M.F. of the cell—



at several temperatures.

The results were as follows :—

Employing	$\frac{N}{2}$	KI solution,	$E_{\text{volts}} = 0.6948 + 0.000305t$
"	$\frac{N}{3}$	"	$E_{\text{volts}} = 0.6932 + 0.000305t$
"	$\frac{N}{10}$	"	$E_{\text{volts}} = 0.6916 + 0.000305t$

the temperature t being given in degrees centigrade.

These values for the E.M.F. require a correction, however, owing to the fact that some of the iodine from the right-hand electrode dissolves in KI, giving tri-iodide (and other poly-iodides, the quantity of which may, however, be neglected). This causes the concentration of the iodine ion I' on the iodine side of the cell to be diminished, and the concentration difference of I' on the two sides of the cell give rise to an E.M.F. e , where—

$$e = RT \log_e \frac{c_1}{c_2}$$

$\frac{c_1}{c_2}$ being the ratio of the I' ion concentrations. With the help of the data of von Ohlendorff, and some experiments of his own on the solu-

bility of iodine in potassium iodide, Fischer succeeded in calculating the value of ϵ for the three cases considered, viz. $\frac{N}{2}$, $\frac{N}{3}$, and $\frac{N}{10}$ KI respectively. The following table contains the corrected value of the E.M.F. and the temperature coefficient $\frac{dE}{dT}$:—

KI Solution.	Temperature, °C.	ϵ .	E corrected.	$\frac{dE}{dT}$ in Cals. per Degree.
$\frac{N}{2}$ {	13.1 28 35.3	0.01708 0.01869 0.02154	0.6817 0.6833 0.6839	} 2.419
$\frac{N}{3}$ {	14.9 24.6 38.6	0.01719 0.01938 0.02327	0.6805 0.6813 0.6817	
$\frac{N}{10}$ {	13.1 23.9 35.4	0.01658 0.01848 0.02118	0.6791 0.6805 0.6807	

Employing these data in the Gibbs-Helmholtz equation, Fischer found for 15° C. (288° abs.) :—

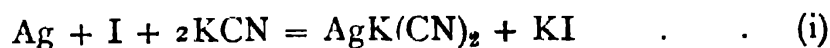
$$\begin{aligned} \frac{N}{2} \text{ KI solution, } U &= 0.6821 \times 23046 - 288 \times 2.419 \\ &= 15,023 \text{ cal.} \end{aligned}$$

$$\begin{aligned} \frac{N}{3} \text{ KI } U &= 0.6806 \times 23046 - 288 \times 1.267 \\ &= 15,315 \text{ cal.} \end{aligned}$$

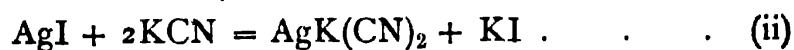
$$\begin{aligned} \frac{N}{10} \text{ KI } U &= 0.6791 \times 23046 - 288 \times 1.66 \\ &= 15,216 \text{ cal.} \end{aligned}$$

The mean value of U is 15,169 cal.

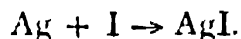
Besides this indirect method of measuring U, Fischer also employed a calorimetric method, precipitation of insoluble salt being avoided by the following very ingenious procedure due to von Wartenberg. As solvent a 3N KCN solution was employed, and in this was placed a known weight of silver powder. The silver is not attacked by the KCN. To the liquid was added a known weight of iodine, the following reaction taking place :—



The heat effect of this reaction was measured. Then using a similar solution of KCN, a known weight of silver iodide was added (no silver powder being present in this case), the resulting reaction being—

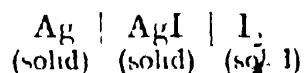


The difference of the heat effects of the reactions (i) and (ii) gives the heat effect desired, *viz.*—



The mean value thus obtained was $U = 14,280$ cals., which agrees pretty closely with the result of the first method. Fischer made use of still another calorimeter method, in which some of Thomsen's data on other salts were employed, the results being less trustworthy. [Note that this is a heat effect at constant volume, since the system does not alter appreciably in volume.]

Now, if we consider the cell—



this represents a condensed system, each phase being a single substance (*no* solution or vapour being present), and we can apply Nernst's heat theorem directly in the form given in equations (1) and (2) above.

[It should be noted that the A or E of this cell is not quite the same as the E or A' of the cell in which KI solution is present. The heat effect in both cases is, however, the same, for, as we have seen, the heat effect as calculated (say by the first method) is independent of the KI concentration, being simply the heat effect of the reaction $\text{Ag} + \text{I} = \text{AgI}$.]

The values of $\beta_0 v$ and of α are known in the case of the three substances Ag, I, and AgI from the atomic and molecular heat measurements of Nernst.

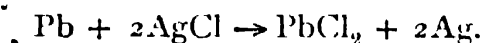
By making use of the values of $\beta_0 v$ and α obtained in this manner, Fischer calculated U for a temperature $T = 288$, finding the value 15,079 calories, a quantity which agrees extremely well with the former values which were obtained for U quite independently of the Nernst heat theorem, or the Nernst-Lindemann atomic heat expression. It is to be remembered that the U and A terms here refer to the reaction between pure solid Ag and solid I_2 , giving solid AgI. A is therefore the affinity which we set out to calculate. The following table contains the values of A and U thus obtained:—

AFFINITY OF SILVER FOR IODINE AT VARIOUS TEMPERATURES.

Temperature, Degrees Absolute	U in Calories per Gram- Atom of Silver	A in Calories per Gram- Atom of Silver
	15,166	15,166
20	15,153	15,173
40	15,136	15,201
60	15,124	15,235
80	15,119	15,274
100	15,114	15,314
140	15,108	15,394
180	15,101	15,477
220	15,093	15,560
260	15,085	15,650
300	15,074	15,733

The accompanying figure (Fig. 16) shows diagrammatically the relative variation of U and A . (On the scale employed the short horizontal section near $T = 0$ over which A and U are identical is not clearly shown.) It will be observed that, in this reaction, the affinity *increases* with increase in temperature, whilst the heat effect or total energy change *decreases*.

A. Magnus (*Zeitsch. Elektrochem.*, **16**, 273, 1910) has carried out a similar investigation of the reaction—



in which the affinity was found to *decrease* as the temperature was raised.

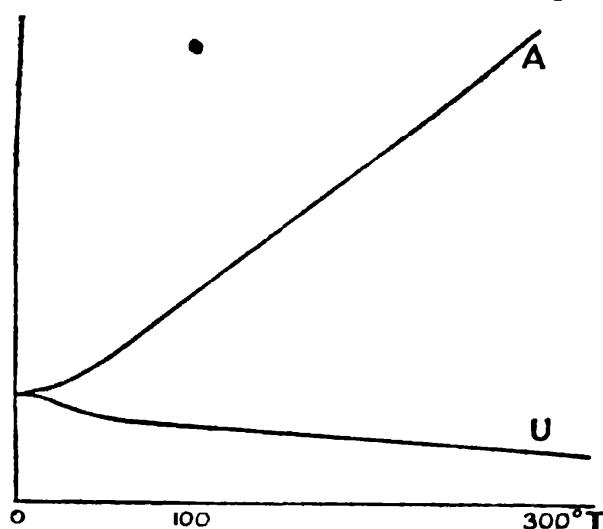


FIG. 16.

In the above illustrations of the Nernst heat theorem, as applied to a reaction between condensed forms, we have allowed for the variation with temperature of the heat capacity of each reacting substance by employing the Nernst-Lindemann equation. On purely theoretical grounds a more rigorous treatment would involve the much less convenient equation of Debye (Chap. III.). So far as numerical values are concerned this would have been of little advantage. The necessity for adopting the Debye equation becomes apparent, however, if we propose to treat the affinity relationships of a given chemical reaction in a condensed system by making use of the approximate formulation of the Nernst heat theorem as expressed in the equations (3_A) and (4_A) of Chap. XIII, Vol. II., *viz.* :—

$$\begin{aligned} U &= U_0 + \beta T^2 \\ A &= U_0 - \beta T^2 \end{aligned}$$

these being the abbreviated forms of equations (3) and (4)—

$$\begin{aligned} U &= U_0 + \beta T^2 + \gamma T^3 + \delta T^4 \\ A &= U_0 - \beta T^2 - \frac{\gamma}{2} T^3 - \frac{\delta}{3} T^4. \end{aligned}$$

According to the formula of Debye, at very low temperatures the internal energy of a condensed substance is proportional to the fourth power of the temperature. Hence for such temperatures it is more exact to write the abbreviated equations, which express the heat theorem for a condensed reaction in the form—

$$U = U_0 + \delta T^4$$

$$A = U_0 - \frac{\delta}{3} T^4.$$

Evidence in favour of this is afforded by the results quoted in the table, Chap. XIII., Vol. II. for the change of monoclinic into rhombic sulphur. Reference to this table shows that the observed values of dU/dT fall more rapidly (as the temperature falls) than would be expected from the values of $2\beta T$, indicating that at low temperatures the power to which the temperature should be raised is greater than the square.

CALCULATION OF THE CHEMICAL CONSTANT OF A MONATOMIC GAS, THE GAS LAW BEING ASSUMED VALID DOWN TO ABSOLUTE ZERO.

[NOTE.—The chemical constant of a substance as originally defined by Nernst is given in Chap. III., Vol. II, namely chemical constant $= \frac{i + \log_e R}{2.3023}$, where i is the integration constant of the equation expressing the variation (with temperature) of the logarithm of the saturated vapour *density* or concentration. It has now become usual in writing expressions for the logarithm of the vapour *pressure* to denote the integration constant by i — i may be conveniently called the “characteristic constant” of a substance—the logarithm of the pressure being to the base e and the pressure itself being expressed in absolute units, whilst on the other hand it is usual to denote the integration constant of the vapour pressure relation by C and to call it the “chemical constant” when the logarithm of the pressure is to the base 10 and the vapour pressure is in atmospheres. We shall keep to this convention in the following section. It is to be understood further that the term $\log$ means $\log_e$; when logarithms to the base 10 are intended these will be written $\log_{10}$.]

The relationship between the Nernst heat theorem and the assumptions underlying the quantum theory become most evident when the chemical constant, or better, the characteristic constant, i —of a monatomic gas in the first instance—is expressed in terms of the quantum theory.

This may be done in more than one way. Thus, Planck's original method shows how the integration constant i is quantitatively related to the *finite* elementary regions (G) of the six-dimensional representative space characteristic of a perfect gas. This is briefly considered in Appendix II., in which it may be noted the symbol α is to be identified with i . The treatment there given is that for a monatomic gas.

A generalised mode of treatment such as that of Planck is less likely, however, to be appreciated than a method in which we keep more closely to the formulation of the heat theorem and the concept of the characteristic constant i as given in Vol. II. With this object, therefore, an alternative method of calculating the characteristic constant in terms of Planck's constant h is given below.

Starting from the Clapeyron equation for vaporisation we have the following relation for the pressure of saturated vapour regarded as a perfect gas—

$$\frac{d \log p}{dT} = \frac{\lambda}{RT^2} \quad (1)$$

where λ = latent heat of vaporisation per mole at the saturation pressure. From the first law of thermo-dynamics as embodied in the expression of Kirchhoff we have also—

$$\lambda = \lambda_0 + \int_0^T C_p dT - \int_0^T C_f dT \quad (2)$$

where λ_0 is the latent heat of vaporisation at absolute zero, C_f is the molecular heat of the condensed form, C_p that of the gaseous phase at constant pressure. Taking C_p to be independent of temperature, equation (1) when integrated becomes—

$$\log p = \frac{\lambda_0}{RT} + \frac{C_p}{R} \cdot \log T - \int_0^T \int_0^T \frac{C_f dT}{RT^2} dT + i \quad (3)$$

where i is the integration or characteristic constant of the substance and cannot be evaluated on a purely thermo-dynamic basis.

On the basis of statistical mechanics it has been shown by Sackur (*Nernst Festschrift*, p. 405 (1912); *Ann. Physik*, **40**, 67 (1913)) and by Tetrode (*Ann. Physik*, **38**, 434; *ib.*, **39**, 255 (1912)) that the characteristic constant or chemical constant of a monatomic substance can be calculated in terms of the molecular weight M and a universal constant, whilst for polyatomic substances it is necessary to know in addition the principal moments of inertia of the molecule. The general form of the expression for the characteristic constant of a monatomic substance, as will be shown later, is—

$$i = i_0 + 1.5 \log M.$$

Although this is deduced, in the first place, for a monatomic gas it is evident that an expression of a similar though more complex form must apply to diatomic gases, since, as has been pointed out in Chapter IV., Eucken's results show that a diatomic gas at sufficiently low temperatures behaves as "thermally monatomic".

The calculation of i or C has been effected also on a statistical mechanical basis by Stern (*Physikal. Zeitsch.*, **14**, 629 (1913); *Zeitsch. Elektrochem.*, **25**, 66 (1919)) who has worked out an expression for the

pressure of a saturated vapour on this basis, and then compared it with equation (3) above and equated the coefficients of like terms.

Before this comparison can be effected, however, it is necessary to evaluate the integral

$$\int_0^T \int_0^T \frac{C_p dT}{RT^2} dT$$

which takes account of the heat capacity of the condensed form. This condensed form we shall regard as a solid and we must therefore treat its heat capacity from the standpoint of the quantum theory, since the integration extends down to absolute zero. This will be taken up later. We shall, in the first place, consider the left-hand side of equation (3), namely the expression which can be obtained for the density and consequently the pressure of a saturated vapour in terms of statistical mechanics.

For this purpose it is not necessary to introduce any quantum considerations since we may imagine that the solid in contact with its saturated vapour is examined under conditions at which the Dulong-Petit law holds good for the solid form. (That statistical considerations have to be introduced at all to evaluate $\bar{v}$ or C is evident at once when we recall that thermo-dynamics only gives the rate of variation of p with T , whilst statistical mechanics permits of the calculation of an absolute value of p .)

We have therefore two distinct problems to solve. First, we have to find an expression for the absolute value of the saturated vapour pressure at some temperature T (which is high enough to permit of the applicability of the Dulong-Petit law to the solid form). In the second place, we have to evaluate the integral

$$\int_0^T \int_0^T \frac{C_p dT}{RT^2} dT$$

which occurs on the right-hand side of equation (3). In the following account Stern's method, with certain abbreviations, is adopted.

Deduction of a Vapour Pressure Formula on the Basis of Classical Statistical Mechanics.

Let us imagine an enclosure of total volume V at the temperature T , containing one gram-molecule, *i.e.* N atoms or molecules of a monatomic substance, where N is the Avogadro constant. The substance exists partly as solid and partly as saturated vapour, the latter being assumed to obey the gas law. The system considered is shown in the accompanying figure.

The solid is supposed to consist of atoms possessing definite equilibrium positions, any distortion being opposed by a restoring force varying as the distance from the position of equilibrium. In such a structure the

heat motion consists of simple harmonic vibrations. In general such vibrations will consist of many different frequencies (e.g. Debye's formula), but to simplify the treatment we shall consider the solid as possessing a single average atomic frequency. Stern (*loc. cit.*) shows that the same vapour pressure formula is arrived at on the simplified basis as on the more general basis.

In order to bring an atom from its equilibrium position in the solid into the gaseous part of the enclosure, that is to vaporise it, an amount of work ϕ_0 is necessary. It would be possible to write $N\phi_0 = \lambda_0$, the latent heat of vaporisation per mole at absolute zero, provided all the atoms at absolute zero were in their equilibrium positions. Since, however, there is the possibility of zero point energy (as is required by the second formulation of the quantum theory), that is, since vibrations are still possible even at absolute zero, it is necessary to write $N\phi_0 = \lambda'_0$ where λ'_0 and λ_0 differ by the amount of the zero point energy.

Considering a given atom at a particular point let us assume that it possesses potential energy ϕ , where ϕ is defined as the work required to bring the atom to the point or position in question. As a zero point for ϕ we shall take the position of equilibrium of the atom in the solid. Then ϕ for any given point in the whole enclosure is equal to the work which is necessary to bring an atom from its position of rest to the point considered. Anywhere in the gas phase ϕ has a constant value, ϕ_0 .

According to Boltzmann the probability W that a given atom occupies a position at which the potential is ϕ is proportional to $e^{-\phi/kT}$, where k is the gas constant per molecule. By the probability term is meant the following. If we consider a given atom and follow its path during a very long period of time t_0 , then in this period it will have occupied all possible positions in the enclosure, i.e. it will have vaporised, moved around in the gas space, recondensed and so on. Let us think now of a portion of the enclosure, which portion we shall denote in the figure by R . The atom referred to will remain, during the course of its wanderings, for a certain length of time t_R inside the volume R . We denote by the probability W_R that fraction of the time of observation t_0 during which the atom remains in R , i.e. W_R is equal to t_R/t_0 . For a sufficiently long observation period t_0 is a quantity independent of the magnitude of t_0 and is the same for all atoms. It is clear that the probability W_R , defined in this manner, depends not only on ϕ , but also on the magnitude

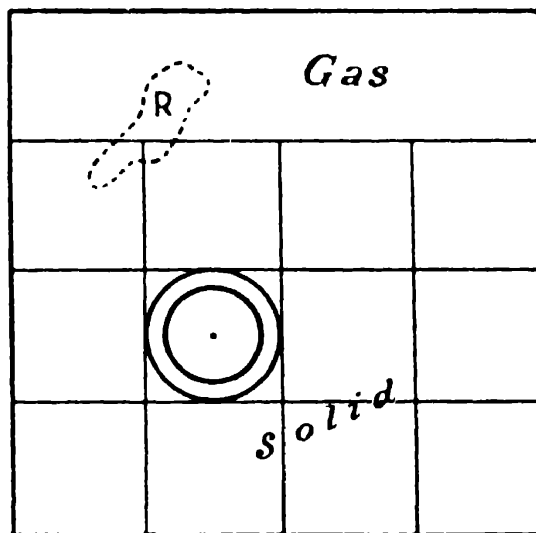


FIG. 17.

of the volume or space R , for an atom will naturally remain longer in R the larger R is, and for a physically infinitely small space dR the probability is simply proportional to dR , because within a very small space ϕ can be regarded as a constant— ϕ being a continuous function of the volume. We can state therefore the Boltzmann principle in the following way:—

$$dW_R = \text{constant } e^{-\phi/kT} dR \quad . \quad . \quad . \quad (4)$$

where $dW_R = t_{dR}/t_0 =$ that portion of the very long time period t_0 during which the atom in question has remained in the space dR , which possesses potential ϕ . The probability W_R for a *finite* portion R of the total volume is therefore—

$$W_R = \text{constant} \int_R e^{-\phi/kT} dR.$$

The value of the constant is obtained simply from the consideration that when $t_R = t_0$, W_R must be unity if the integration has been carried out over the entire volume V . Denoting the constant by I we have—

$$1 = I \int_V e^{-\phi/kT} dR.$$

We now proceed to calculate for a given atom the probability W_g that it is to be found in the gaseous phase, and likewise the probability W_f that it is to be found in the solid phase. If V_g is the volume of the gaseous phase we have, since the potential is everywhere constant and has the value ϕ_0 —

$$W_g = I \int_{V_g} e^{-\phi_0/kT} dR = I \cdot V_g \cdot e^{-\phi_0/kT} \quad . \quad . \quad . \quad (5)$$

In order to calculate W_f , we imagine the solid made up of a number of cells, the equilibrium position of an atom being at the centre of a cell (*cf.* Fig. 17). We now proceed to calculate the probability, W_c , that the atom under “observation” is to be found in a particular cell, *e.g.* the second cell on left of the middle row in the figure. For this purpose we imagine two spheres radii r and $r + dr$ drawn round the equilibrium position. In the space between the two spherical surfaces of infinitely small thickness dr and of volume $4\pi r^2 dr$, the potential $\phi(r)$ has everywhere the same value, $\phi(r)$ being the work which is necessary to bring the centre of gravity of the atom from its equilibrium position to a distance r away. Setting the opposing force as proportional to r , namely $a^2 r$, where a^2 is a proportionality factor, we have—

$$\phi(r) = \int_0^r a^2 r dr = a^2 r^2 / 2$$

and the probability that the atom under observation is to be found in this space between the two spherical surfaces is—

$$I e^{-a^2 r^2 / 2kT} 4\pi r^2 dr.$$

Hence the probability W_r that the atom is to be found anywhere within a sphere of radius r measured from the equilibrium position is given by—

$$W_r = \int_0^r e^{-a^2 r^2 / 2kT} 4\pi r^2 dr.$$

Now what we want is not the probability W_r of the atom finding itself inside a sphere enclosing the equilibrium position, but rather the probability W_z of the atom being anywhere in the whole cell. To find an expression for the latter we make use of the fact that a^2 is a quantity the magnitude of which can be calculated from the specific heat, melting-point, optical or elastic properties, since a^2 is defined by the relation—

$$a^2 = (2\pi\nu)^2 m,$$

where ν is the characteristic frequency of vibration and m the mass of the atom. The important thing is that a^2 is thus found to be a very large quantity, so that the term $e^{-a^2 r^2 / 2kT}$ is practically zero, *except when r is very small*. Hence it is only over the range where r is very small (the range already considered when obtaining an expression for W_r) that the probability of finding the atom has any sensible value; for by hypothesis the atom is one experiencing a restoring force which varies simply as the distance, *i.e.* at a distance greater than r_0 , say, from the equilibrium position, an atom of the kind considered is practically never found. It is evident that we are considering the solid under the condition at which the Dulong-Petit law holds, for this law can be deduced on the assumption of the above law of force. Hence the probability W_z is identical with W_{r_0} where

$$W_r = \int_0^{r_0} e^{-a^2 r^2 / 2kT} 4\pi r^2 dr = 4\pi \int_0^{x_0} e^{-a^2 r_0^2 x^2} x^2 dx,$$

where $\frac{a^2 r_0^2}{2kT} = x^2$ and $\frac{a^2 r_0^2}{2kT}$

If, now, x_0 is very great compared with unity—

$$\int_0^{x_0} x^2 e^{-x^2} dx =$$

Hence

$$W_z = \int_0^{x_0} x^2 e^{-x^2} dx = \frac{1}{2} \left(1 - e^{-x_0^2} \right)$$

This represents the probability that the centre of gravity of an atom is to be found within a given cell. If n_f is the number of atoms composing the solid phase, n_f likewise represents the number of cells into which we imagined the solid phase to be divided, and the probability W_f that the atom under observation is to be found in the solid phase is given by—

$$W_f = n_f W_z = \int_0^{x_0} x^2 e^{-x^2} dx \quad (6)$$

The probability W_g of finding the atom in the gaseous phase has already been given by equation (5). On combining the two equations we obtain—

$$\frac{W_g}{W_f} = \frac{V_g e^{-\phi_0/kT}}{n_f \cdot \left(\frac{2\pi kT}{a^2}\right)^{3/2}}.$$

This is the ratio of the time periods during which the atom under observation remained in the gaseous and solid phases respectively. Since we have made no special assumptions about the atom which has been under observation it is evident that W_g/W_f has the same value for all the atoms. If, therefore, instead of following out the path of a particular atom over a long period of time we consider all the atoms at a given moment of time, the ratio W_g/W_f gives us the ratio of the number of atoms in the gaseous to those in the solid phase. That is

$$\frac{n_g}{n_f} = \frac{W_g}{W_f} = \frac{V_g e^{-\phi_0/kT}}{n_f \cdot \left(\frac{2\pi kT}{a^2}\right)^{3/2}}$$

or
$$\frac{n_g}{V_g} = \left(\frac{a^2}{2\pi kT}\right)^{3/2} \cdot e^{-\phi_0/kT}.$$

But $\frac{n_g}{V_g}$ = number of gaseous atoms per unit volume.

Hence,

$$p = \frac{n_g}{N} \cdot \frac{RT}{V_g} = \frac{n_g}{V_g} \cdot kT = \left(\frac{a^2}{2\pi}\right)^{3/2} \cdot \frac{e^{-\lambda'_0/kT}}{(kT)^{1/2}}.$$

Substituting the value $(2\pi v)^2 m$ for a^2 , we obtain finally for the pressure of the saturated vapour—

$$p = \frac{(2\pi m)^{3/2} v^3}{(kT)^{1/2}} \cdot e^{-\lambda'_0/kT}$$

or, since $Nm = M$, the gram-molecular weight,

$$p = \frac{(2\pi M)^{3/2} v^3}{N \sqrt{RT}} \cdot e^{-\lambda'_0/kT} \quad (7)$$

It is to be remembered that this expression for the pressure of saturated vapour obtained on the basis of classical statistical mechanics holds only for those temperatures at which the Dulong-Petit law applies to the atomic heat of the solid form.

We have now to compare equation (7) with equation (3). Equation (7) can be written thus—

$$\log p = -\frac{\lambda'_0}{RT} - \frac{1}{2} \log T + \log \frac{(2\pi M)^{3/2} v^3}{NR^{1/2}} \quad (7a)$$

Equation (3) may also be written, since for a monatomic gas at constant pressure $C_p = \frac{5}{2} R$ —

$$\log p = - \frac{\lambda_0}{RT} + \frac{5}{2} \log T - \frac{C_p}{RT^2} dT + i \quad (3a)$$

To enable the comparison of (3a) with (7a) to be carried out it is necessary to evaluate the integral which occurs in (3a). Stern does this by applying the equation of Debye for C_p . Equation (3a) thus becomes—

$$\log p = - \frac{(\lambda_0 + \sum_{\frac{1}{2}}^{3N} h\nu)}{RT} - \frac{1}{2} \log T + \log \frac{h^3 \nu^3}{k^3} + i.$$

In this expression the summation Σ is to be taken over the whole $3N$ degrees of freedom postulated as present by Debye. k is the gas constant per molecule.

Comparing this with (7a) and equating the coefficients of like terms, we obtain—

$$\lambda'_0 = \lambda_0 + \sum_{\frac{1}{2}}^{3N} h\nu \quad (8)$$

$$\log \left(\frac{h^3 \nu^3}{k^3} \right) + i = \log \left(\frac{(2\pi M)^{3/2} \nu^3}{N^{3/2} k^{1/2}} \right)$$

$$\text{Whence} \quad i = \log \left(\frac{(2\pi m)^{3/2} h^{5/2}}{h^3} \right) \quad (9)$$

Equation (8) expresses the important result that the work λ'_0 , required to vaporise N atoms at absolute zero, is not equal to the latent heat of vaporisation λ_0 , but is greater than this by the quantity $\sum_{\frac{1}{2}}^{3N} h\nu$. Stern regards this as evidence for the existence of zero point energy as already mentioned, the atoms even at absolute zero not being all in their equilibrium positions, but on the average possessing energy $\frac{1}{2} h\nu$ per atom per degree of freedom.

Equation (9) is the solution of the problem of the calculation of the characteristic constant of a *monatomic* gas. As regards the numerical evaluation of i Stern points out that an accurate method is available, involving the elimination of h and k , if we accept Bohr's expression for the Rydberg constant R_ν (*cf.* Chap. V.), which is a quantity determinable with great accuracy from, say, the series spectrum of hydrogen. According to Bohr—

$$R_\nu = \frac{2\pi^2 e^4 \mu}{h^3} = \frac{2\pi^2 F^4 \mu}{N^4 h^3}$$

where e is the charge on an electron, μ the mass of an electron, and E the electrochemical equivalent. Referring to equation (9) we can write:

$$i = \log \left(\frac{(2\pi m)^{3/2} \cdot k^{5/2}}{h^3} \right) = \log \left(\frac{(2\pi)^{3/2} \cdot R^{5/2}}{N^4 h^3} \right) + \frac{5}{2} \log M$$

or
$$i = i_0 + \frac{5}{2} \log M \quad (10)$$

Further
$$\frac{1}{N^4 h^3} = \frac{R_y}{2\pi^2 E^4 \mu}$$

Hence
$$i = \log \left(\frac{(2\pi)^{3/2} \cdot R^{5/2}}{N^4 h^3} \right) = 2.3026 \log_{10} \left(\frac{2^{1/2} \cdot R^{5/2} \cdot R_y}{\pi^{1/2} \cdot E^4 \mu} \right).$$

Substituting the following numerical values—

$R = 8.315$ ergs; $R_y = 3.921 \times 10^{16}$;
 $E = 2.895 \times 10^{11}$ electrostatic units; $\mu = 0.902 \times 10^{-27}$ gram,
 we obtain—

$$i_0 = 2.3026 \times 4.417 = 10.17,$$

whence—

$$i = 10.17 + \frac{5}{2} \log M.$$

This expresses i in absolute units. On the other hand, the chemical constant C is expressed in terms of logarithms to the base 10 with the pressure in atmospheres. Since one atmosphere = 1.0132×10^6 dynes per cm.² we can write—

$$C = \frac{i}{2.3026} - \log_{10} 1.0132 \times 10^6$$

or
$$C = 4.417 + \frac{5}{2} \log_{10} M - 6.0057$$

or, finally,
$$C = -1.587 + \frac{5}{2} \log_{10} M = C_0 + \frac{5}{2} \log_{10} M.$$

The value of C_0 calculated by Nernst is -1.608 . The difference between this and the value given by Stern is due to slightly different values being taken for the term $N^4 h^3$.

The “experimental” values of C_0 obtained from vapour pressure data, in the case of argon and hydrogen, by Nernst (*Grundlagen des neuen Thermodynamik*, 1918) and by Egerton (*Phil. Mag.*, **39**, 1 (1920)) in the case of mercury, cadmium, and zinc, are given in the following table.—

THE CHEMICAL CONSTANT.

Substance	C.	M.	C_0
H ₂ . . .	-1.23 ± 0.15	2.016	-1.68 ± 0.15
Ar . . .	$+0.75 \pm 0.06$	39.88	-1.65 ± 0.06
Hg . . .	$+1.820 \pm 0.032$	200.6	-1.633 ± 0.032
Cd . . .	$+1.65 \pm 0.31$	112.4	-1.42 ± 0.31
Zn . . .	$+1.23 \pm 0.26$	65.37	-1.49 ± 0.26

The weighted mean value for C_0 , greatest stress being laid on the accuracy of the mercury value, least stress on the zinc and cadmium

values, is, according to Egerton: -1.622 ; a value which differs by about 2 per cent. from that calculated by Stern, *viz.* -1.587 .

The problem of the precise dimensions of the chemical constant has been considered in some detail by Lindemann. This is summarised in Appendix VIII.

CALCULATION OF THE CHEMICAL CONSTANT OF A GAS ON THE BASIS OF THE DEGRADATION THEORY OF GASES.

The calculation of the chemical constant by the method outlined below depends essentially on the direct applicability of Nernst's heat theorem to gaseous systems, such applicability being rendered possible by the assumption of a degraded state at very low temperatures. This method of treatment was first effected by Nernst (*Zeitsch. Elektrochem.*, **22**, 185, 1916; *Grundlagen des neuen Warmesatzes*, 1918). An account of the degradation theory itself has been given in the section bearing that title in Chap. IV. of this volume. We shall have occasion, in what follows, to make use of certain of the equations which are given in the section referred to. For convenience sake the same numbering will be employed.

As already shown, the degradation theory requires that the molecular heat of a gas—in the first place a monatomic gas—at finite volume shall decrease towards zero as the absolute zero of temperature is approached (*cf.* equation (2) of section referred to). This is analogous to the behaviour of a condensed system. The rapidity with which this happens, *i.e.* the slope of the C_p curve, depends on the volume occupied by the gas, the greater the volume the smaller the frequency of rotation of the molecules and consequently the more quickly does C_p rise as the temperature rises, *i.e.* the lower is the temperature at which C_p reaches its upper limit $3\frac{1}{2} \cdot R$. If we are considering the case, for example, in which one gram-molecule of the gas occupies 22.4 litres the frequency term is of the order of 10^9 , whilst the frequency characteristic of a solid, it will be recalled, is of the order 10^{12} . For such a case, therefore, the molecular heat of the solid would become negligible at a temperature at which the molecular heat of the degraded gas would still be sensible. Although this relative behaviour is essentially a function of the dilution of the gas, we shall consider, in what follows, that the volume of the gas, in general, is such that at the temperature considered the molar heat of the solid is negligible compared with that of the degraded gas.

On the basis of the degradation theory the behaviour of the gas is such that at constant volume a lowering in temperature (condensation being precluded) causes the pressure to fall not to zero but to a finite value, the "Nullpunktsdruck" which remains constant for any further fall in temperature. That is, over a certain temperature region we can write—

$$\text{limit } dp/dT = 0 \text{ for } T = 0$$

for the degraded gas.

Since at the same time the molecular heat becomes zero in the neighbourhood of absolute zero it follows that—

$$\text{limit } dU/dT = 0 \text{ for } T = 0.$$

In this manner Nernst generalises his heat theorem, which is now seen to be applicable to all states of matter.

The limiting pressure referred to above is (as we have already seen in the relevant section of Chap. IV., equation (5)), given by—

$$p_0 = h^2 N^{5/3} / 4\pi m V^{5/3}$$

not only at absolute zero but also for a small temperature interval above zero. Thus, keeping the volume of the gas constant, its pressure is independent of the temperature over the range referred to. This behaviour is in marked contrast to the behaviour of a gas if the gas law is obeyed down to absolute zero. For the sake of clearness we shall consider this point from another aspect.

Consider a single gas expanding between the volumes V_1 and V_2 . If the gas law were obeyed down to absolute zero we would have—

$$\text{whence, } A = RT \log V_2/V_1, \quad \text{limit } dA/dT = R \log V_2/V_1 \text{ for } T = 0.$$

Obviously the limit of dA/dT is not zero. Similarly, for the more general case of a chemical process it can be shown (*cf.* Nernst, *Grundlagen*, p. 156) that the limit dA/dT is not zero, provided the gas law is obeyed. Hence Nernst's heat theorem is not applicable to gaseous systems obeying the gas law down to absolute zero. The degradation theory is essentially a denial of the validity of the gas law at exceedingly low temperatures. It is to be remembered that we are here dealing with finite volumes. If the volume of the gas were practically infinite the gas law would apply almost to absolute zero, *i.e.* there would be no degradation except in the limit. This case is met with approximately in the behaviour of saturated vapours for which, owing to their extreme rarefaction at very low temperatures, the gas law is regarded as applicable almost to absolute zero.

Let us consider a physico-chemical process, namely, the process of condensation of one gram-molecule of a gas to the solid form, the gas being in the degraded state and occupying therein a volume V at a very low temperature T . V is large compared with the volume of the condensed form produced as a result of the change. Let λ_0 be the heat which would be evolved in the condensation of an infinitely dilute gas at absolute zero. In the actual case considered, in which condensation takes place from a finite volume V , let us suppose that U_0 represents the change (decrease) in the total energy at absolute zero. We then have—

$$U_0 = \lambda_0 + \frac{3}{2} N h\nu = \lambda_0 + \frac{3}{2} \cdot N \cdot \frac{h^2 N^{2/3}}{4\pi M V^{2/3}} \quad (\alpha)$$

This expression will be evident when it is recalled that the internal energy of the gas at absolute zero occupying volume V is $\frac{3}{2}N\hbar\nu$ (cf. section on degradation theory, Chap. IV.), where ν is the frequency of molecular rotation. The same mass of gas at infinite dilution possesses no analogous energy term, since $\nu = 0$ for $V = \infty$. Hence $\frac{3}{2}N\hbar\nu$ is the amount of energy which would be evolved in altering the volume of the gas from V to infinity. In the latter state the heat of condensation is, by definition, λ_0 . The equation (a) follows at once. As a rule $\frac{3}{2}N\hbar\nu$ is small compared with λ_0 . Thus, for one mole of hydrogen occupying 22.4 litres at absolute zero, $\frac{3}{2}N\hbar\nu$ is 0.211 cal., whilst $\lambda_0 = 250$ cal. approximately.

At a temperature T above zero we then have for the change in total energy—

$$U = \lambda_0 + \frac{3}{2}N \cdot \frac{\hbar^2 N^{2/3}}{4\pi m \bar{V}^{2/3}} + E,$$

where E is identical with $\int_0^T C_v dT$ and, as shown by equations (1) and (2) of relevant section, Chap. IV.—

$$E = \frac{5}{2}R \cdot \frac{\beta_0 \nu}{e^{\beta_0 \nu/1} - 1} - \frac{3}{2}N \cdot \frac{\frac{\hbar^2 N^{2/3}}{4\pi m V^{2/3}}}{e^{N^{2/3} \hbar^2 / 4\pi m V^{2/3}} - 1}.$$

For the reasons already given the term analogous to E for the solid state can be neglected compared with E for the gaseous (even the degraded) state.

Applying Nernst's heat theorem to the act of condensation envisaged above, we have—

$$- \int_0^T \frac{U}{T^2} dT$$

$$\text{or} \quad A = U_0 - \int_0^T \frac{U}{T^2} dT \quad (\beta)$$

$$\text{since} \quad U = U_0 + E \quad (\gamma)$$

The relative positions of the A and U curves for the process considered are shown in the accompanying figure. It will be observed that at absolute zero itself the free and total energy terms (A_0 and U_0) are identical (as the Second Law requires) and the variation of these quantities with temperature are also identical (and zero) for a certain range above $T = 0$. The extent of the range over which $dA/dT = dU/dT = 0$ is determined by the value of V , namely, V_1 and V_2 , the volume of the gas initially considered.* If V_1 is larger than V_2 , then, as pointed out in Chap. IV., $C_{v1} > C_{v2}$ and the U_{v1} curve rises more steeply than the U_{v2} curve. Consequently the A_{v1} curve falls more rapidly than the A_{v2} curve. Actually the value of U_0 (or of A_0) depends

on the value of V , as is shown by equation (a), but this alteration is not shown in the figure, since U_0 is mainly determined by the term λ_0 . Equations (a), (β), and (γ) serve to determine completely the variation of A and U with temperature.

We have now to consider the case of the *saturated* vapour. The equilibrium between the vapour and the condensed form is given by the equation—

$$A' \doteq -pV = -RT,$$

the negative sign denoting that the process considered is condensation.

As already mentioned, the gram-molecular volume of the saturated vapour is so very large at low temperatures that the gas law is obeyed at such temperatures. The points at which the A_{v_1} and A_{v_2} curves

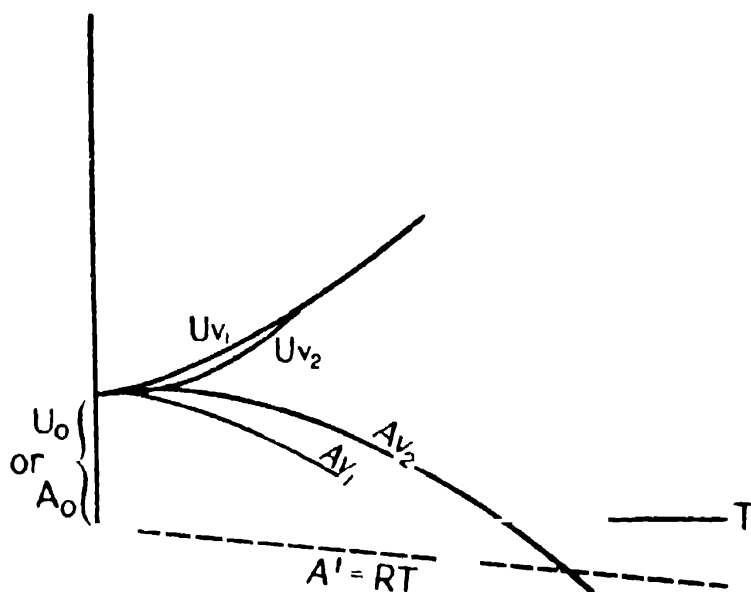


FIG. 18.

intersect the $A' = RT$ line denote the temperatures at which V_1 and V_2 just correspond to the molar volumes of saturated vapour. Since V_1 is greater than V_2 , and since the molar volume of saturated vapour increases as the temperature falls, it follows that the A_{v_1} curve cuts the A' curve at a lower temperature than does the A_{v_2} curve.

If A' and V were known at all temperatures it follows from the relation $A' = -pV$ that p , the saturation pressure, would also be known. For the saturated vapour, *i.e.* for the point of intersection of the A and A' curves, we can write $A' = A$. Consequently equation (β) will serve to define A' and ultimately, therefore, p itself, provided we attach to the V term (which occurs in the E term of equation (β)) the molar volume of *saturated* gas at the temperature considered. In applying equation (β) in this manner we notice, in the first place, that—

$$\int_0^T \frac{E}{T^2} dT = \frac{3}{2} RT \log \left(\frac{h^2 N^{2/3}}{e^{4\pi m k T^{3/2}}} \right) - \frac{3}{2} N \cdot \frac{h^2 N^{2/3}}{4\pi m V^{2/3}}$$

and since $U_0 = \lambda_0 + \frac{3}{2}N \cdot \frac{h^2 N^{2/3}}{4\pi m V^{2/3}}$

we can write : $A = \lambda_0 + \frac{3}{2}RT \log \left(e^{\frac{h^2 N^{2/3}}{4\pi m k T V^{2/3}}} - 1 \right).$

Setting $A = A' = - RT$ for some temperature above zero we have

$$- RT = \lambda_0 + \frac{3}{2}RT \log \left(e^{\frac{h^2 N^{2/3}}{4\pi m k T V^{2/3}}} - 1 \right).$$

Writing

$$\frac{h^2 N^{2/3}}{4\pi m k T V^{2/3}} = x$$

it follows that when x is small, i.e., when V is very large (as will be the case for *saturated* vapour)—

$$e^x - 1 = xe^x \text{ to a very close approximation.}$$

This follows, since $xe^x = x \left(1 + \frac{x}{2} + \dots \right) = x + \frac{x^2}{2} + \dots$

$$\text{Hence, } - RT = \lambda_0 + \frac{3}{2}RT \log \left(\frac{h^2 N^{2/3}}{4\pi m k T V^{2/3}} \cdot e^{\frac{h^2 N^{2/3}}{4\pi m k T V^{2/3}}} \right).$$

$$\text{But, } \frac{h^2 N^{2/3}}{4\pi m k T V^{2/3}} = \frac{h^2 p^{2/3}}{4\pi m k^{5/3} T^{5/3}}, \text{ since } V = \frac{NkT}{p}.$$

$$\begin{aligned} \text{Hence, } \frac{3}{2}RT \log \frac{h^2 N^{2/3}}{4\pi m k T V^{2/3}} &= RT \log \frac{h^3 p}{(4\pi m)^{3/2} k^{5/2} T^{5/2}} \\ &= RT \log p - \frac{5}{2}RT \log T - RT \log \frac{(4\pi m)^{3/2} k^{5/2}}{h^3} \end{aligned}$$

$$\begin{aligned} \text{Hence } - RT &= \lambda_0 + \frac{3}{2}N \cdot \frac{h^2 N^{2/3}}{4\pi m V^{2/3}} + RT \log p - \frac{5}{2}RT \log T \\ &\quad - RT \log \frac{(4\pi m)^{3/2} k^{5/2}}{h^3} \end{aligned}$$

$$\text{or, } \log p = - \frac{\lambda_0 + \frac{3}{2}N \cdot \frac{h^2 N^{2/3}}{4\pi m V^{2/3}}}{RT} + \frac{5}{2} \log T - 1 + \log \frac{(4\pi m)^{3/2} k^{5/2}}{h^3}$$

and since $-\log_e e = -1$ we obtain finally

$$\log p = - \frac{\left(\lambda_0 + \frac{3}{2}N \cdot \frac{h^2 N^{2/3}}{4\pi m V^{2/3}} \right)}{RT} + \frac{5}{2} \log T + \log \left(\frac{(4\pi m)^{3/2} k^{5/2}}{e h^3} \right) \quad (8)$$

where e is the base of the natural logarithms. Equation (8) is the expression obtained for the vapour pressure-temperature curve on the basis of Nernst's heat theorem as applied to vapours through the medium of the degradation theory.

We have now to compare this expression with that given by the classical laws of thermodynamics, namely, the Clapeyron equation,

which in its simplest integrated form (with omission of the term for the energy of the condensed phase) becomes—

$$\log p = -\frac{\lambda_0}{RT} + 2.5 \log T + i,$$

where i is the integration constant.

On comparing this with equation (δ) they are seen to be identical except for the additional term in equation (δ), namely, $\frac{3}{4}N \cdot \frac{k \sqrt{2/3}}{4\pi m V^{2/3}}$. This, however, as already pointed out, is of the nature of a small correction and may be neglected. Hence on equating like terms we find—

$$i = \log \left(\frac{(4\pi m)^{3/2} k^{5/2}}{e h^3} \right) \quad (e)$$

Equation (e) is the expression obtained on the basis of the degradation theory for the characteristic constant of a monatomic substance. The chemical constant is related in a simple manner to i , as shown in the previous section.

Quite apart from the degradation theory we have already seen (foregoing section, equation g) that an expression may be obtained for i , namely—

$$i = \log \left(\frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right).$$

The two expressions are similar, except that in the first we find the term $\log \frac{(4\pi)^{3/2}}{e}$ in place of $\log (2\pi)^{3/2}$, which occurs in the second.

Numerically they are almost identical. Thus $\log \frac{(4\pi)^{3/2}}{e} = 1.215$, whilst $\log (2\pi)^{3/2} = 1.197$. Experimental measurement is not as yet (1923) sufficiently refined to distinguish between these two values. Nernst regards the numerical factor of Sackur, Tetrode, and Stern as probably more correct than that given by the degradation theory, but at the same time points out the advantage of the latter mode of treatment in that it brings out how the integration constant depends upon the energy content of the gas itself.

On the other hand, Lindemann (*Phil. Mag.*, **39**, 21, 1920) has subjected the chemical constant (*i.e.* the characteristic constant i) to a careful examination, the results of which are adverse to the degradation theory. Lindemann, in fact, shows how the chemical constant may be eliminated, and the vapour pressure expressed in an entirely new way, namely, in terms of the pressure of complete (black-body) radiation. This suggests in turn that thermal radiation must play a fundamental part in chemical change. Lindemann expresses it thus: "It is therefore suggested that the chemical constant may express the interaction of matter and complete radiation rather than requiring that a gas can

CHEMICAL CONSTANT OF POLYATOMIC GASES

assume only a finite number of possible microphases at a given temperature, pressure, and volume." An account of Lindemann's examination of the chemical constant is given in Appendix VIII.

The Chemical Constant of Polyatomic Gases.

The expression which has been obtained for the integration constant i , namely—

$$i = \log \left(\frac{(2\pi m)^{3/2} h^{5/2}}{h^3} \right) \quad (1)$$

applies only to perfect monatomic gases. In the case of an ideal polyatomic gas it is necessary to take into account the moments of inertia corresponding to the degrees of freedom in respect of molecular rotation. For a diatomic gas we are concerned with a single moment of inertia, I ; for molecules containing three or more atoms all three moments of inertia, I , J , and K , have to be introduced. Obviously in the case of a monatomic gas, since rotation is impossible, such terms do not enter.

The mode of expressing the characteristic constant i of a polyatomic gas was first given by Sackur and by Tetrode (*loc. cit.*) and later by Schames (*Physikal. Zeitsch.*, **21**, 38, 158, 1920) and by Tolman (*Journ. Amer. Chem. Soc.*, **43**, 866, 1921). Schames (*loc. cit.*, p. 156) has further attempted to calculate the electrical moment of a dipolar molecule from the moment of inertia, I .

For a diatomic molecule it is found that—

$$i = \log \left(\frac{(2\pi m)^{3/2} \cdot h^{7/2} \cdot 8\pi^2 I}{h^6} \right) \quad (2)$$

and for a molecule containing three or more atoms—

$$i = \log \left(\frac{(2\pi m)^{3/2} \cdot h^4 \cdot 8\pi^2 \sqrt{IJK} \cdot (2\pi)^{3/2}}{h^6} \right) \quad (3)$$

As regards numerical quantities, the values of I for the diatomic gases oxygen, carbon monoxide, and nitrogen, obtained from the characteristic constant i with the aid of equation (2), are given in the second column of the following table:—

Gas.	$I \times 10^{40}$, From Equation (2).	$I \times 10^{40}$, Laski.
O ₂	31.2	7.51
CO	10.07	—
N ₂	9.91	10.06

The third column contains the values of I calculated by Laski (*Physikal. Zeitsch.*, **20**, 269 (1919)) on the basis of the Bohr-Debye model from specific heat data at very high temperatures. The agreement is very

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bad for oxygen, but satisfactory for nitrogen. It may be mentioned that from a consideration of the spacing of the lines of the cyanogen band spectrum, which is attributed to molecular nitrogen, it has been calculated that $I = 14 \times 10^{-40}$, a result in good agreement with the above. In the case of hydrogen—which would be expected to possess a value of I considerably smaller than those quoted above—Sommerfeld has deduced from the spacing of the many-lined spectrum of the gas that $I = 1.85 \times 10^{-41}$, whilst from the chemical constant, by means of equation (2), one obtains $I = 1.0 \times 10^{-41}$, and from the early Bohr-Debye model, $I = 2.9 \times 10^{-41}$. The last value is undoubtedly too great, that is, the structure of H_2 is more compact than would be anticipated on the early Bohr basis, now discarded by Bohr himself.

For the triatomic molecule H_2O the value of $\sqrt{IJK}$ is found to be 0.94×10^{-40} , whilst Hettner has calculated from the rotation spectrum of water vapour the value 1.38×10^{-40} on the basis of Planck's first theory and 2.48×10^{-40} on the basis of the second. The cause of the discrepancy is unknown.

As regards the calculation of electric moments, in the case of the H_2O molecule, to which Schames attributes a certain structure in which the hydrogen atoms lie in the same plane with the oxygen atom above this plane, the calculated electric moment is 5.52×10^{-18} , whilst that obtained by Jona (*Physikal. Zeitsch.*, **20**, 14 (1919)) is 1.87×10^{-18} . The agreement is only correct as regards order of magnitude.

Tolman (*loc. cit.*), deals with the analysis of the characteristic constant from the point of view of entropy, but on a wholly different basis from that adopted by the other authors mentioned. Tolman's method involves an application of his principle of similitude or relativity of size. Since the method is in effect an extension of the theory of dimensions it is not possible to analyse it completely, no information being given regarding the purely numerical constants.

MASS ACTION EQUILIBRIUM IN SOLUTIONS FROM THE STANDPOINT OF INFRA-RED RADIATION.

(Cf. F. Kruger, *Zeitsch. Elektrochem.*, **17**, 453, 1911.)

The problem to be considered is the relation of the ionisation constant of the solute to the dielectric constant of the solvent.

The radiation density in a medium depends upon the cube of the refractive index n as well as upon other factors. Further, on the basis of the classical electro-magnetic theory of light, the refractive index is connected with the dielectric constant D by the relation $n^2 = D$. Hence the radiation density is proportional to the dielectric constant raised to the power $3/2$. It follows that in media of high dielectric constant, such as water, the radiation density is correspondingly high. Thus, D for water is approximately 81, and $81^{1.5} = 730$. Hence for long waves the radiation density in water at ordinary temperatures is 730 times the radiation density in a vacuum, where $D = 1$. Krüger

considers the case of a dissolved electrolyte, and assumes that only a fraction of all the ions vibrate, but that those which do vibrate at all possess the theoretical amount of vibrational energy required by classical statistical mechanics, *i.e.* $3RT$ per "active" gram-ion. The high dielectric constant, according to Krüger, also sets a number of the charged atoms in the undissociated molecules of the solute into vibration again with the amount of energy per "active" gram-atom¹ required by statistical mechanics. The higher the radiation density of a medium, that is, the higher its dielectric constant, the greater will be the number of molecules of solute activated in this sense, and hence the greater the degree of ionisation of the solute. This is suggested as the basis, in terms of radiation, of the relation known as the Nernst-Thomson rule.

We now pass to the consideration of the mass action equilibrium resulting from such ionisation. Krüger carries out a thermodynamic work process in which allowance is made for the difference in radiation density arising from the fact that two *different* solvents or media are employed.

Let us consider two media, dielectric constants D_1 and D_2 , the media being capable of mixing in all proportions. We might imagine a cylinder containing one solvent placed above the other with a mixture layer between the two. In each solvent let us suppose that there is one gram-molecule of a binary electrolyte dissolved, the ionisation constant of the electrolyte being K_1 in solvent I. and K_2 in solvent II.; $K_1 > K_2$. The following cyclic process is then carried out. In medium I. one mole of the undissociated electrolyte ionises. The ions are brought by the aid of semi-permeable membranes into solvent II. where they unite, the undissociated molecule being returned to solvent I. The osmotic work of transferring the *material* is as follows: let C_0, C_1, C_2 be the equilibrium concentrations of the undissociated molecules and the ions respectively of the solute in solvent I.; C'_0, C'_1, C'_2 are the corresponding quantities in solvent II. The osmotic work of the cycle is then given by—

$$A = RT \left(\log \frac{C_1}{C'_1} + \log \frac{C_2}{C'_2} - \log \frac{C_0}{C'_0} \right) = RT \log \frac{K_1}{K_2}.$$

In this process a certain amount of radiation is absorbed when ionisation occurs in solvent I., and the same amount is given out when the ions unite in solvent II.² We have to deal therefore with a transport of *radiation* at the same time as we deal with a transport of material. The radiation is transported from a region of higher radiation density (solvent I.) to a region of smaller radiation density (solvent II.). The work of transporting the radiation may be calculated in the following manner:—

¹ In the present case the "critical increment" of the undissociated molecule is very small (*cf.* Chap. VII., section dealing with Thermal Reactions).

² Krüger assumes here that the heat of the reaction is the same in both solvents. This, in general, will not be the case.

Let us consider a certain amount of radiation, *i.e.* the amount required to "activate" one gram-molecule of the electrolyte, and let us suppose that this radiation is enclosed in a membrane impermeable to radiation. The radiation exerts a pressure—"the pressure of light"—upon the membrane tending to expand it. This pressure is proportional to the density of the radiation. It is known that the pressure π of the radiation is related to the volume ϕ by an expression which is quite analogous to Boyle's law for gases, *viz.* $\pi\phi = k$.

[NOTE.—There is a serious difficulty here, as the expression assumes the temperature of the radiation is constant. If it is isolated its temperature cannot remain constant on expansion or compression.]

If we accept this expression it follows that the maximum work gained in expanding the radiation from π_1 to π_2 , corresponding to the radiation densities u_1 and u_2 , is $k \log \pi_1/\pi_2$. Further, on the electro-magnetic theory of light, $\pi = u/3$, so that the radiation work is $k \log u_1/u_2$. The density terms are proportional to the cube of the refractive indices or to the 1.5 power of the respective dielectric constants D_1 and D_2 . Hence the radiation work can be written as—

$$k \log (D_1^{3/2}/D_2^{3/2}).$$

We have now to determine the constant k . "Let us assume that each vibrating ion [charged atom] in the undissociated molecule possesses three degrees of freedom, that is, each ion possesses $3/2RT$ of kinetic energy and a like amount of potential energy, making in all $3RT$ per ion, or $6RT$ for the two ions in the molecule reckoned per gram-molecule—each gram-molecule when it dissociates requires on the average an amount of energy $6RT$ which is drawn from the radiation." Hence—

$$u\phi = 6RT, \quad \text{radiation density}$$

and since $\pi = u/3$, it follows that—

$$\pi\phi = 2RT. \quad \bullet \quad \text{STANDPOINT OF}$$

Substituting this in the expression for the work done by the radiation, we obtain—

$$A = 2RT \log (D_1^{3/2}/D_2^{3/2}) = RT \log D_1^3/D_2^3 \quad \text{con}$$

The ionisation equilibrium is defined by the equality of radiation work terms.¹

We obtain therefore—

$$RT \log \frac{K_1}{K_2} = RT \log \frac{D_1^3}{D_2^3} \quad \text{osmotic pressure}$$

or
$$K_1/K_2 = D_1^3/D_2^3.$$

¹ Naturally if the solvent had been the same in both cases, and if the solutions are dilute, the radiation work term would be zero, and we are left with the osmotic work terms. The cycle would then reduce to the familiar one employed to deduce the law of mass action, *i.e.* K_1 would be identical with K_2 .

MASS ACTION EQUILIBRIUM IN SOLUTIONS

That is, on the basis of the assumptions made by Krüger, we would expect the ionisation constant to vary as the cube of the dielectric constant of the system. In order to test this conclusion it is convenient to put it into another form. If γ_1 and γ_2 are the degrees of ionisation at the dilutions V_1 and V_2 respectively in the two solvents, then—

$$\frac{K_1}{K_2} = \frac{\gamma_1^2}{(1 - \gamma_1)V_1} \cdot \frac{(1 - \gamma_2)V_2}{\gamma_2^2} \cdot \frac{D_1^3}{D_2^3}$$

If we choose the concentrations, *i.e.* the dilutions, of the solute in the two solvents in such a manner that the degrees of dissociation are the same, the above relation becomes—

$$V_2/V_1 = D_1^3/D_2^3$$

or $D^3\sqrt{V} = \text{constant for a given value of } \gamma.$

This relation had already been discovered as a purely empirical one by Walden (*Zeitsch. phys. Chem.*, **54**, 129 (1906)) as a result of measurements carried out with tetra-ethylammonium iodide in a number of solvents. The following are a few of Walden's results. In each case the dilution term V denotes the dilution at which the degree of ionisation has the value assigned to it at the head of the table:—

$\gamma = 0.83.$			
Solvent.	Dielectric Constant.	Dilution V in Litres	$D^3\sqrt{V}.$
Water	80	32	254
Nitromethane	40	200	234
Furfural	39	200	230
Acetonitrile	36	320	245
Methyl sulfocyanide	36	270	233
„ alcohol	32.5	400	240
Propionitrile	27.2	800	253
Acetyl acetone	26	1000	260
Acetic anhydride	17.9	2000	226
Benzyl cyanide	16.7	3200	246
Anisaldehyde	15.5	3100	226
Benzaldehyde	14.5	4100	252
$\gamma = 0.91.$			
Water	80	110	383
Furfural	39	800	365
Nitromethane	40	800	371
Acetonitrile	36	1000	358
Methyl alcohol	32.5	2000	365

As will be seen, the relation is borne out approximately. Krüger deals with the possible causes of the deviations. Of these the most

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important is connected with the relation $n^2 = D$, which is known to hold only for very long waves. It is probable that the wave-lengths chiefly concerned in ionisation, although belonging to the infra-red region, do not conform to this relation. It is known that n varies with the wave-length when the latter is short, *i.e.* the ultra-violet, visible, and the short infra-red regions. Hence the values of D are to a considerable extent arbitrary, the values not being strictly comparable. Thus the value obtained for the dielectric constant will depend very largely on whether there exists an absorption band at the wave-length employed in the dielectric constant apparatus. In the case of water it is considered that the high value obtained is partly due to the fact that water possesses a band for the electro-magnetic waves usually employed. Further, Kruger's assumptions are possibly not correct in all cases. Thus, it is very surprising that the results quoted should be as satisfactory as they are, for the electrolyte is *strong*. Nevertheless the deduction, so far as it goes, indicates that radiation plays a rôle in ordinary chemical processes. Kruger shows further how an empirical relationship of Walden, according to which "saturated solutions of one and the same electrolyte in various solvents possess the same degree of ionisation," can be deduced on the radiation basis. For details regarding this and other matters the original paper of Kruger must be consulted.

THE HEAT OF REACTION. HABER'S RELATION.

In Chap. VII. we have dealt with the rate of a thermal reaction and the velocity constant from the point of view of the quantum theory. In the case of a unimolecular reaction in a homogeneous system the variation of the velocity constant with the temperature is given by the expression—

$$d \log k / dT = Nh\nu / RT^2$$

where ν is the characteristic vibration frequency, or head of the absorption band, of the decomposing substance. If the reaction be a reversible one, the resultant being characterised by the frequency ν' , the corresponding velocity constant being k' , we have—

$$d \log k' / dT = Nh\nu' / RT^2.$$

Hence

$$\frac{d \log k/k'}{dT} = \frac{Nh(\nu - \nu')}{RT^2}.$$

But $k/k' = K$, the equilibrium constant. Hence we obtain the relation—

$$d \log K / dT = Nh(\nu - \nu') / RT^2.$$

At the same time the statistical mechanical expression of Marcelin and Reic gives the relation—

$$d \log K / dT = (E - E') / RT^2$$

where E is the critical increment of the reactant, E' that of the resultant. On comparing these expressions with the van't Hoff isochore, *viz.*—

$$d \log K/dT = - Q_v/RT^2$$

where $-Q_v$ is the heat absorbed per stoicheimetric quantity of the reactant transformed or decomposed, we obtain the relation—

$$-Q_v = (\text{heat absorbed}) = Nh(\nu - \nu') = E - E'$$

or, heat evolved in the reaction = critical quantum of the resultant minus the critical quantum of the reactant.

In the case of reactions involving several reactants and resultants we may generalise the above expression, and write—

$$\text{Heat evolved} = \Sigma Nh'_{\text{resultants}} - \Sigma Nh'_{\text{reactants}}.$$

This expression, deduced however by a totally different method, was first given by Haber (*Ber. Deutsch. phys. Ges.*, **13**, 1117, 1911). It may therefore be called the Haber expression for the heat effect. The above mode of deduction is that given by the writer (*Trans. Chem. Soc.*, **111**, 457, 1917).

In the above formulation the heat of reaction at constant volume has been expressed as the difference of the critical quanta or the difference of the critical increments of the resultants and the reactants. The heat effect at constant volume is also thermodynamically defined as the difference of the mean internal energies of the reactants and resultants. To see that these two definitions are concordant we may proceed in the following manner.

Let us consider the simplest type of reaction, *viz.* $A \rightleftharpoons B$. The various energy terms involved in the process are represented in the accompanying diagram (Fig. 19). The ordinates denote internal energy, the length ab corresponding to the mean value U_1 of the internal energy possessed by one gram-molecule of the substance A, and similarly the length de represents the mean energy U_2 of the substance B. Before one gram-molecule of A, possessing the average internal energy U_1 , can become reactive its internal energy must rise to the point c by the addition of the critical increment E_1 . At this stage the gram-molecule possesses the energy $(U_1 + E_1)$. It may now change into one gram-molecule of B, with an evolution of energy denoted by the dotted line ce . The gram-molecule now possesses the mean energy de , or U_2 characteristic of the substance B. In passing from c to e the energy emitted is $(U_1 + E_1) - U_2$. In

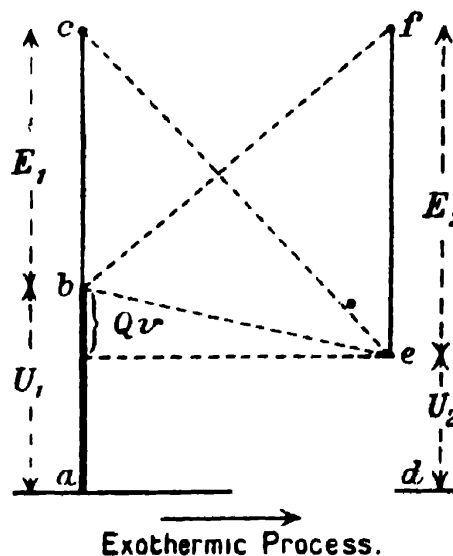


FIG. 19.

passing from the mean state b to the mean state e the total energy evolved is $(U_1 + E_1 - U_2) - E_b$, or $U_1 - U_2$. The total energy evolved in passing from e to b is $(U_2 + E_2 - U_1) - E_b$, or $U_2 - U_1$. This expresses the fact that if the reaction is exothermic it necessarily is endothermic in the reverse direction¹.

When a molecule is in the critical state it is impossible to say whether it belongs to the system A or to the system B. That is, the critical state is common to both A and B. If E_c denotes the total critical energy—not the critical increment— E_c will have the same value for the A and B molecules alike. This is indicated in the diagram by the lines ac and df being of equal length. From the above considerations it follows that—

$$\begin{aligned} E_c &= U_1 + E_1 = U_2 + E_2 \\ \text{Hence } U_1 - U_2 &= E_2 - E_1 = Q_v = N\hbar(\nu' - \nu) \end{aligned}$$

In writing Q_v as the difference between the critical quanta of the resultant and reactant we have really assumed that Q_v is a constant independent of temperature. This, of course, cannot be exact, as it would mean that $dU/dT = 0$, or that the sum of the molecular heats of reactants is equal to those of the resultants. The above radiation expression is therefore an approximation. In this connection it may be mentioned that a recent investigation of equilibria in the gaseous state has led Schiffer (*Proc. Akad. Wetenschap Amsterdam*, **19**, 636, 1917) to the conclusion that the variation in Q_v with temperature is a negligible quantity in general, i.e. "the experimental error in the determination of K is always such as to render meaningless any attempt to allow for the variation of Q with T ". This *practical* conclusion does not effect the question, however, of the true variation of Q with T .

The integrated expression for K on the above radiation basis takes the approximate form—

$$\begin{aligned} \log_e K &= - \frac{N\hbar(\nu' - \nu)}{RT} + \text{constant}, \\ \text{or } \log_e K &= - \frac{N\hbar\Sigma(\nu' - \nu)}{RT} + \text{constant}, \end{aligned}$$

where ν' refers to resultants, ν to reactants, and K is so defined that the equilibrium concentration terms of the resultants appear in the numerator.

In connection with the magnitude of the heat of reaction observed in some cases a point of importance arises. Take the case of the union of hydrogen and oxygen gases to form water vapour in which a very large amount of heat is evolved. On the basis of activation and critical increments no particular difficulty arises since the actual process

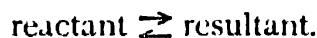
¹ Note that on the above mechanism the system never passes along a line such as bc , except in the case in which the critical state of a substance is identical with its normal state. This appears to be the case for atoms formed by dissociation of a gaseous molecule, the dissociation being accompanied by an *absorption* of heat which is identical with the critical increment of the molecule. The critical increment of the atoms appears to be zero.

is attributed to activated molecules and not to those possessing the normal or average amount of energy. On the other hand, the thermodynamic definition of heat effect at constant volume would require in the above case that the average internal energy of the hydrogen and oxygen was at least as great as the heat evolved in the formation of water. The magnitude of this heat effect is such, however, that it could not possibly be accounted for in terms of the heat capacities or integration of the C_v/T values from absolute zero up to the temperature of reaction. To maintain the thermodynamic definition as a physical reality it would seem necessary to postulate with Planck a zero point energy and to assume that this can manifest itself in the chemical change. Whether this is the case or not is by no means clear since on the basis of active molecules the thermodynamic statement is formally true although the actual process differs from that implied in the thermodynamic statement.

THE LE CHATELIER-BRAUN PRINCIPLE FROM THE POINT OF VIEW OF THE RADIATION HYPOTHESIS.

(Cf. Lewis, *Trans. Chem. Soc.*, **115**, 710, 1919.)

Consider the reversible reaction—



Let us suppose that the reaction from left to right is endothermic. Then, in accordance with the principle of mobile equilibrium, an increase in temperature will favour the resultants.

From the point of view of radiation, the fact that the above process is endothermic means that the critical increment of the resultant is less than that of the reactant. This follows from the quantum-heat expression—

heat evolved =

critical increment of resultant – critical increment of reactant,

or heat evolved = $Nh(\nu_2 - \nu_1)$, where N is the Avogadro number and h is Planck's constant. In the case considered, it follows that the critical frequency ν_2 of the resultant is less than the critical frequency ν_1 of the reactant.

Let us consider the above equilibrium at two different temperatures, T_1 and T_2 , where T_1 is less than T_2 . For the short infra-red region (which has already been shown to be of significance for reactions which proceed with measurable velocity at the ordinary temperature), as well as for the visible and ultra-violet regions, the radiation density corresponding with the frequency ν_1 at T_1 is—

$$\frac{8\pi h \nu_1^3}{c^3} e^{-h\nu_1/kT_1},$$

and at T_2 the density is—

$$\frac{8\pi h\nu_1^3 n^3}{c^3} e^{-h\nu_1/kT_2},$$

where c is the velocity of light in a vacuum.

If T_1 and T_2 are not very far apart, and especially if the reacting system is gaseous, the refractive index term n will be practically the same at both temperatures.

The fractional increase in the radiation density, due to the rise in the temperature from T_1 to T_2 at the frequency ν_1 , is given approximately by—

$$\frac{\frac{8\pi h\nu_1^3 n^3}{c^3} (e^{-h\nu_1/kT_2} - e^{-h\nu_1/kT_1})}{\frac{8\pi h\nu_1^3 n^3}{c^3} e^{-h\nu_1/kT_1}}$$

which is equal to

$$\left(e^{\frac{h\nu_1}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} - 1 \right).$$

Similarly, for the fractional increase in the radiation density at the frequency ν_2 we obtain—

$$\left(e^{\frac{h\nu_2}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} - 1 \right).$$

Since by hypothesis ν_1 is greater than ν_2 , it follows from the above expressions that the fractional increase in the radiation density at the frequency ν_1 is greater than that at the frequency ν_2 . Hence at the higher temperature the radiation density of the type absorbable by the reactant (ν_1) has increased *relative* to that absorbable by the resultant (ν_2).

On the radiation hypothesis of chemical reactivity, it is assumed that the rate of decomposition is directly proportional to the radiation density. For both frequencies, the rise in temperature has caused an increase in the radiation density, but the increase is relatively greater for the higher frequency (ν_1) than it is for the lower frequency (ν_2). It follows, therefore, that at the higher temperature both the reactant and the resultant react or decompose more rapidly than they do at the lower temperature. This is in agreement with experiment. What is more important, however, is that the reactant decomposes at a relatively faster rate than the resultant, because the radiation density of the reactant is relatively increased with respect to that of the resultant. Hence as the temperature is raised, the existence of the resultant, in the above case, is favoured more than that of the reactant, and the equilibrium position shifts over towards the right. Had the reaction been exothermic, the relative positions of ν_1 and ν_2 would have been reversed, with the result that the equilibrium concentration of the reactant would have increased relatively to that of the resultant.

These conclusions are identical with those which are arrived at on the basis of the principle of Le Chatelier and Braun. In so far as this is concerned the radiation hypothesis is in agreement with the thermodynamic generalisation.

APPENDIX I.

MAXWELL'S DISTRIBUTION LAW AND THE PRINCIPLE OF EQUIPARTITION OF ENERGY.

BY JAMES RICE, M.A.

THE aim of mechanics is the description of motion. We seek to specify the position of every part of a system of bodies at every instant. The most direct way of doing this would be to express all the necessary geometrical co-ordinates of the system as known functions of the time. To this end the laws of motion are applied to the special features and environment of each system, and a series of differential equations are obtained which, among other quantities, involve the first and second differential coefficients of each co-ordinate with respect to the time, *i.e.* the velocities and accelerations. If the mathematician can solve for us the particular differential equations arrived at, we have attained our object for that system. Many special cases of considerable interest have proved amenable to mathematical treatment, but, at present, no solution for the general case exists.

In the phrase, "system of bodies," we must be definite as to the meaning to be attached to the word "body". In physics and chemistry, a single body is a system, *i.e.* a collection of molecules, which are in themselves discrete, if minute bodies. Indeed, the molecule itself is a system of atoms and, on present views, the atom is a system of nuclei and electrons. Even if we regard a body of fluid or solid material as a system of molecules alone, without concerning ourselves about its internal structure, the complexity of description involved in a complete account of molecular motion is so great that it becomes necessary to introduce the mathematical theory of probability. We are no longer concerned with an *exact* solution of the dynamical problem, by which one could predict with certainty the position and motion of each molecule at a given instant; instead we endeavour to find the law of distribution of the co-ordinates and velocities of the molecules, so as to be able to state, with but small possibility of error, that at a given instant such and such a fraction of the molecules will occupy such and such a portion of the space filled by the body, and have velocities lying between such and such limits. It is this feature which characterises a problem as one of statistical mechanics.

In dealing with a system of molecules, the co-ordinates referred to above are naturally the Cartesian co-ordinates of the centres of each molecule referred to a definite set of axes; but it should be borne in mind

that in general dynamics the word "co-ordinate" is used to indicate any geometrical quantity which serves to specify the position and configuration of the parts of a system, the least number of such co-ordinates which is necessary to specify the system completely being, in fact, its number of "degrees of freedom". Thus, if we attempt to treat the problem of a system of molecules which are themselves systems of atoms, we should have to introduce further geometrical magnitudes to those mentioned above, which would define the position of each atom relative to the centre of its corresponding molecule.

As regards the velocities of the individual molecules, there are two ways open to us to specify such a velocity, both as regards its magnitude and its direction. We may give the three components of the velocity parallel to the three axes of co-ordinates, or we may give the actual speed combined with some convenient way of indicating its direction. The following is a simple method of defining direction:—

Conceive of a sphere of unit radius. Every direction in space is parallel to some radius of the sphere. Consequently a point P on the surface of the sphere can be said to represent a direction in space, *viz.* the direction parallel to OP where O is the centre of the sphere. Any direction and its opposite are of course represented by diametrically opposite points on the sphere. In statistical work we have to classify directions into groups, and one convenient way of doing this is as follows: Draw a series of planes perpendicular to a given diameter of the unit sphere, and meeting the diameter in points which divide the diameter into an exact number, say m , of equal parts. These planes divide the surface into a series of zones, and it is well known that these zones have equal areas, *viz.* $4\pi/m$, 4π being in fact the entire area of the sphere whose radius is unity. Still further subdivide the surface by a number of planes, say n , each containing the diameter and each one making with its neighbouring planes, angles which are all equal to an aliquot part of 2π radians, *viz.* $2\pi/n$ radian. This new family of planes cuts the surface of the sphere in great circles which subdivide each zone in equal parts, each part being four-sided and equal in area to $4\pi/mn$. (The parts round the ends of the diameter are three-sided but have the same area). If we call this area ω , then the number of such elements of area is mn or $4\pi/\omega$. It will prove convenient presently to classify directions into groups such that all the directions in one group correspond to points in one superficial element of the representative sphere. In the nature of things no finite limit can be assigned to the number of directions in one group, no matter how small the elements of area are made by closer and closer subdivision by the planes of "latitude and longitude," but of course closer subdivision and an increase in the number of groups involves closer and closer limits to the angular differences between any pair of directions in one group.

The problem in statistical mechanics which has received the greatest attention concerns the statistics of a body of gas enclosed in a fixed volume and in a steady state with regard to such properties as temperature pressure and density. Here, among other things, answers have

been found to such questions as refer to distribution of the positions and velocities of the molecules, the mean number of molecular collisions per second, the mean free path, the connection between these quantities and the pressure, temperature, viscosity, rate of diffusion, etc., of the gas. We proceed to quote some known results concerning the distribution of the molecules in position and in velocity.

As regards the positions of the molecules, we conceive the enclosure to be subdivided into a great number, say n , "physically small" volumes or cells. This means that each cell is supposed too small to be dealt with separately by an experimental apparatus and yet large enough to contain an enormous number of molecules. As it is known that the number of molecules in one cubic mm. of a gas at N.T.P. is about 3×10^{16} , this condition is easily complied with. Suppose we have altogether N molecules in the enclosure, then the average number of molecules per cell is N/n which is assumed to be a large number. Suppose we express the actual number of molecules in any cell as $N/n \cdot (1 + \delta)$, where δ is the fractional variation of this molecular density from the mean molecular density N/n , and may be positive or negative.

It can be proved that there is an enormous probability against the possibility of δ acquiring values of an order of magnitude greater than the order of $1/N$. As N is enormous, this practically means that there is an enormous probability in favour of *uniform* distribution of the molecules in position. It should be noted as a feature of this statistical proposition that the proof of it does not prove the *impossibility* of the number of molecules in any cell deviating seriously from the mean number; it proves that such a state is extremely improbable, and that the dynamical conditions which would produce it occur so infrequently and exist for so brief a time that actual demonstration of its existence would elude our experimental arrangements.

When we come to deal with the distribution of the molecules in terms of velocity, we do not find this uniformity of distribution. Taking the question of speed alone, apart from questions of direction, there is certainly a theoretical upper limit to the possible speed attainable by any one molecule; it is in fact the speed which that molecule would have if it possessed the entire energy of the gas, the other molecules being absolutely at rest. Such a speed is, however, far beyond any practical limit; although there is no dynamical impossibility in the state of affairs pictured, there is an enormous probability against it.

The application of statistical methods to this problem leads to the view that certain speeds are more privileged than others. Thus there is one speed such that there are at a given instant more molecules possessing velocities within, say, one foot per second of this speed than there are molecules possessing speeds within one foot per second of any other speed; and if we choose speeds smaller and smaller or larger and larger than this "maximum probability" speed, these speeds are less and less privileged, until, when we arrive at zero speed or at speeds very great compared with the maximum probability speed, the probability of their occurrence is very small indeed. There are, however,

no privileged *directions*, all directions of motion being equally likely. This rough statement will serve to introduce the mathematical law of the distribution of velocities, first formulated by Maxwell and often stated in the words: "the law of distribution of the velocities among the molecules of a gas in the steady state is the law of errors".

As a matter of fact there are two ways of stating Maxwell's Law, one of which assumes a velocity to be measured by its components parallel to the Cartesian axes, the other way assumes that a velocity is to be measured by its magnitude and direction on the plan explained above (the unit sphere device). In the former case the law of the distribution is *for each component* similar to the normal law of errors, but in the latter case the law of distribution of the *speeds* is not the normal law of errors. Let us take the first method of formulation.

Considering an enormous number of molecules, N , it can be shown that in the steady state those of them which at one instant have velocities whose X components lie between narrow limits, say u and $u + du$, are in number equal to—

$$NAe^{-\gamma u^2} du$$

where A and γ are constants to be determined shortly. This number constitutes a fraction $Ae^{-\gamma u^2} du$ of the whole. It should be carefully observed that the group of velocities here dealt with are not necessarily close to each other in magnitude and direction: it is only their X components which are close to each other in magnitude, no restriction is so far imposed on the Y and Z components.

Of this limited number there will be at the same instant a certain fraction which have their Y components between v and $v + dv$, this fraction being in fact $Ae^{-\gamma v^2} dv$; so that the number whose X and Y components are between u and $u + du$, and v and $v + dv$ respectively,

$$\text{or} \quad \frac{NA^2 e^{-\gamma u^2} du \cdot e^{-\gamma v^2} dv}{NA^2 e^{-\gamma(u^2 + v^2)} du dv}$$

A similar step gives the number of those whose X , Y , and Z components are at one instant within the limits u to $u + du$, v to $v + dv$, and w to $w + dw$ respectively, as—

$$NA^3 e^{-\gamma(u^2 + v^2 + w^2)} du dv dw \quad (1)$$

We can calculate the constant A in terms of γ ; for if we integrate for all values of u , v , and w from $-\infty$ to $+\infty$, we must get N .

$$\text{Hence} \quad N = NA^3 \int_{-\infty}^{+\infty} e^{-\gamma u^2} du \cdot \int_{-\infty}^{+\infty} e^{-\gamma v^2} dv \cdot \int_{-\infty}^{+\infty} e^{-\gamma w^2} dw.$$

We can also calculate γ in terms of the total kinetic energy of the molecular motion. For the fraction of the whole, *i.e.* fractional number of the whole number of molecules, which is represented by—

$$NA^3 e^{-\gamma(u^2 + v^2 + w^2)} du dv dw$$

have each kinetic energy $\frac{1}{2}m(u^2 + v^2 + w^2)$ where m is the mass of a molecule.

Hence the total kinetic energy is—

$$\frac{1}{2}NA^3m \int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dw \cdot (u^2 + v^2 + w^2) \cdot e^{-\gamma(u^2 + v^2 + w^2)} du dv dw.$$

Leaving aside the constant factor for the moment, we see that the triple integral is the sum of three triple integrals, one of which, for instance, is—

$$\int_{-\infty}^{+\infty} u^2 e^{-\gamma u^2} du \cdot \int_{-\infty}^{+\infty} e^{-\gamma v^2} dv \cdot \int_{-\infty}^{+\infty} e^{-\gamma w^2} dw.$$

Now it is known that—

$$\int_{-\infty}^{+\infty} u^2 \cdot e^{-\gamma u^2} du = \frac{1}{2} \sqrt{\pi/\gamma^3}$$

and the two remaining integral factors in the above chosen integral have already been evaluated. Hence the selected member of the three triple integrals has the value $\frac{1}{2} \sqrt{\pi^3/\gamma^3}$, and the other two have each the same value. Hence the total kinetic energy is—

$$\frac{3}{2}NA^3m \sqrt{\pi^3/\gamma^3}, \text{ i.e. } \frac{3}{2}Nm/\gamma; \text{ since } A = \sqrt{\gamma/\pi}.$$

Now we could conceive the molecules all moving with one uniform velocity as a rigid body, for instance, and that velocity such as to give the same kinetic energy as that due to the gaseous motion. Denote the magnitude of this hypothetical velocity by $\bar{c}$, and we have—

$$\begin{aligned} \frac{1}{2}Nm\bar{c}^2 &= \frac{3}{2}Nm/\gamma, \\ \gamma &= 3/\bar{c}^2. \end{aligned}$$

This particular speed $\bar{c}$ is not the true average speed, nor is it the maximum probability speed referred to above (its relation with these will be given presently); it is in fact a speed whose square is the average of the squares of the molecular speeds at one instant, and on that account is called the root-mean-square or r-m-s-speed. Assuming that this r-m-s-speed is known, we formulate Maxwell's Law in one way thus:—

Of a great number N of gaseous molecules in a steady state with an r-m-s-speed $\bar{c}$, the number whose velocity components at one instant lie between the limits u to $u + du$, v to $v + dv$, w to $w + dw$, is—

$$\frac{27}{4} \cdot e^{-3(u^2+v^2+w^2)/\bar{c}^2} du dv dw \quad (2)$$

and we see that any one particular component, say u , enters into this expression in a manner similar to the way the error x enters into the expression for the normal law of errors *viz.*, $\int e^{-h^2x^2} dx$.

We can employ a geometrical method of representing this law. Imagine that u , v , w are chosen to be the Cartesian co-ordinates of a point in a three-dimensional diagram, which we will refer to as the velocity diagram. The origin O of the co-ordinates in this diagram, represents absolute rest, while any other point P represents a velocity whose magnitude is given by the length OP and whose direction is the direction of OP . Let us write c for the length OP , *i.e.*

$$c = \sqrt{u^2 + v^2 + w^2}$$

gives the actual speed corresponding to the point P . Now suppose we represent, as it were, every molecule by a point in this diagram, *i.e.* each point represents the velocity—not the position—of some molecule, so that we have therefore N points marked in the diagram; these points will, of course, move about with lapse of time, because of the changing velocity of the corresponding molecule. The expression (2) states the volume distribution of these points at a given instant. Thus, taking $du dv dw$ to be an element of volume of the velocity diagram the “density” of the points around the point representing zero speed, *i.e.* representing the condition of rest, is—

$$N \sqrt{27/8\pi^3} \bar{c}^3.$$

Around any point representing a speed c (with no restriction as to direction), *i.e.* around a point lying anywhere on a sphere of radius c with its centre representing rest, the density of the points is—

$$N \sqrt{27/8\pi^3} \bar{c}^3 \cdot e^{-3c^2/2\bar{c}^2} \quad (3)$$

So the density of the swarm of points diminishes in this exponential manner as we recede from the point representing rest. The reader is warned against drawing the erroneous conclusion that there are at any moment more molecules in the gas at rest, or very nearly so, than there are those possessing any other assigned speed or near to it. The fallacy involved in such an inference will be pointed out presently.

An element of volume in the velocity diagram represents what is called an “extension-in-velocity,” just as an element of volume in actual space occupied by a gas is an “extension-in-position.” Thus we may refer to expression (3) as the “density-in-velocity” of the molecules about any velocity of the magnitude c .

We can readily pass to the second manner of formulating Maxwell's Law, and in so doing clear away the possibility of misconception referred to a few lines back. Suppose we wish to find the number of molecules whose *speeds* (*i.e.* merely velocity magnitudes) are at any moment between the limits c and $c + dc$, but with no limits placed on their directions of motion. We must obviously find the number of points in our velocity diagram which lie between spherical surfaces of radii c and

$c + dc$. The volume of the elementary region of this diagram is $4\pi c^2 dc$, and the point density in the region is given by (3). Hence the number sought is—

$$4\pi N \sqrt{27/8\pi^3} c^2 \cdot e^{-3c^2/2\bar{c}^2} \cdot dc \quad (4)$$

The expression (4) has, for a given value of the differential element of speed, dc , its maximum value for a value of c which makes—

$$c^2 e^{-3c^2/2\bar{c}^2}$$

a maximum. By the usual methods of the calculus it appears that this value of c is: $\sqrt{2/3}\bar{c}$ or $0.816\bar{c}$; so that there are more molecules at an instant possessing speeds within, say, one foot per second of this speed than of any other assigned speed. That is, $0.816\bar{c}$ is the speed with "maximum probability".

We can now deal with the fallacious inference mentioned above. Let us consider a velocity with speed c and a *definite* direction whose direction angles are α , β , and γ . The velocity has then the components—

$$c \cos \alpha, c \cos \beta, c \cos \gamma.$$

Now, undoubtedly, there are more molecules whose velocities have components between $0, 0, 0$ and du, dv, dw than there are molecules with velocity components between $c \cos \alpha, c \cos \beta, c \cos \gamma$ and $c \cos \alpha + du, c \cos \beta + dv, c \cos \gamma + dw$. This is a just inference from equation (3); but this statement is not true if we remove the condition of *definiteness* from the angles α, β , and γ and allow them to take any possible values. The removal of this restriction does not alter the *speed* limits, but it multiplies the number in the second group enormously. From the point of view of the velocity diagram, the representative points do undoubtedly cluster more densely around the origin of the diagram, and less and less densely around a point gradually receding from the origin, but the actual law of distribution provides for the number of points which lie in a thin spherical shell of definite thickness, increasing as we go out to a shell of average radius $0.816\bar{c}$ and then decreasing as we go still further. From the origin to $0.816\bar{c}$ the increasing volume of the shell more than compensates the decreasing density of the points; further on it fails to do so.

We can modify expression (4) so as to deal with velocities having defined limits of direction. Expression (3) shows us that the density-in-velocity is a function of speed only; hence there are no privileged directions. So of those molecules which at an instant have speeds between c and $c + dc$, the number whose directions of motion are restricted to the directions represented by points on a superficial element ω of the unit sphere constitute a fraction $\omega/4\pi$. Multiplying expression (4) by this fraction, we find that the number of molecules so restricted as to speed and direction is—

$$\omega N \sqrt{27/8\pi^3} c^2 \cdot e^{-3c^2/2\bar{c}^2} \cdot dc \quad (5)$$

If we wish to find the number of molecules which have speeds within limits finitely separated we must integrate (4) or (5) between the limits. Thus the number unrestricted as to direction, with speeds between c_1 and c_2 , is—

$$4\pi N \sqrt{27/8\pi^3 \bar{c}^3} \int_{c_1}^{c_2} c^2 \cdot e^{-3c^2/2\bar{c}^2} \cdot dc \quad (6)$$

Expression (6) can be much simplified by introducing instead of the speed c the ratio which this speed bears to the maximum probability speed $\sqrt{2/3} \cdot \bar{c}$.

Call this ratio x so that—

$$c = \sqrt{\frac{2}{3}} \cdot \bar{c} \cdot x$$

and hence

$$dc = \sqrt{\frac{2}{3}} \cdot \bar{c} \cdot dx.$$

On introducing these expressions into (6) we find after a little rearrangement that the number of molecules whose speed ratios lie between x_1 and x_2 is—

$$4N/\sqrt{\pi} \cdot \int_{x_1}^{x_2} x^2 e^{-x^2} dx \quad (7)$$

[In (7) we might refer to x as the speed, if we took the maximum probability speed as the unit of speed.]

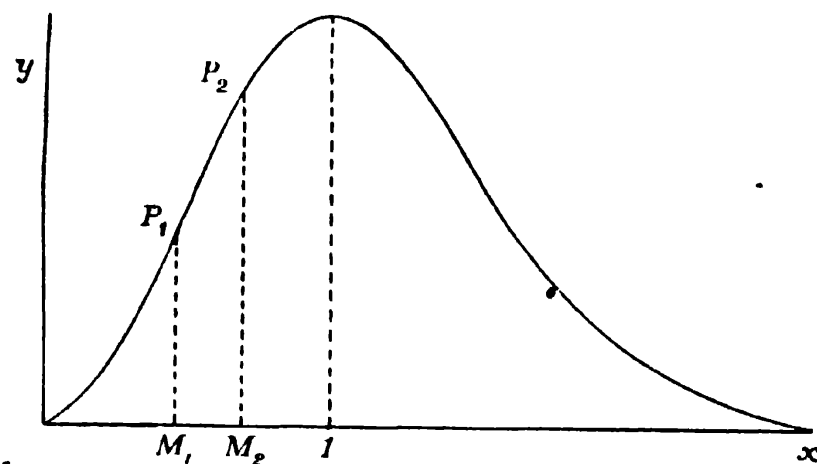


FIG. 20.

The properties of the integral in (7) can be most readily exhibited by means of Fig. 20, which is the graph of the curve—

The graph begins at the origin O ; y rises to a maximum value $1/e$ (or 0.37 approximately) when $x = 1$; the curve then descends asymptotically to the axis of x , y reaching as low a value as 0.02 when $x = 2.5$, showing that all but a very small fraction of the molecules have speeds at any moment less than two and a half times the maximum probability

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speed (which corresponds to x equal to unity) or practically twice the r-m-s-speed. In fact, the fraction of the molecules whose speed ratios lie between x_1 and x_2 is given by: $4/\sqrt{\pi}$ area of $P_1M_1M_2P_2$, where $OM_1 = x_1$ and $OM_2 = x_2$. By methods of analysis or quadrature of a carefully drawn graph numerical values can be obtained. The following table from Meyer's *Kinetic Theory of Gases* (translated by Baynes) illustrates the point:—

Of 1000 molecules of oxygen at 0°C. , whose r-m-s-speed is known (by methods to be explained presently) to be 461.2 metres per second—

13 to 14 molecules have speeds below					100 metres per second.		
81	82	"	"	from	100 to 200	"	"
166	167	"	"	"	200 " 300	"	"
214	215	"	"	"	300 " 400	"	"
202	203	"	"	"	400 " 500	"	"
151	152	"	"	"	500 " 600	"	"
91	92	"	"	"	600 " 700	"	"
76	77	"	"	above	700	"	"

The table shows that all but about 10 per cent. of the molecules have speeds between one-half and double the r-m-s-speed. It thus appears that despite the possibility of any definite molecule acquiring a speed enormous in comparison with the average, the probability of it doing so is exceedingly remote. It should also be observed in illustration of the point dealt with earlier, that the number possessing quite low speeds is also very small.

The kinetic theory of gases explains the pressure of a gas as the result of molecular bombardment, and connects the pressure and temperature of the gas with its mean molecular kinetic energy. The actual relations are as follows:—

If ρ grams per c.c. is the density of the gas, and p dynes per square cm. its pressure, it can be shown that—

$$p = \frac{1}{3}\rho\bar{c}^2$$

where $\bar{c}$, the r-m-s-speed, is measured in cms. per second. If p and ρ are known, this enables us to calculate $\bar{c}$, as, for example, in the table just given. If E is the energy of motion of a molecule—

$$E = \frac{1}{2}m\bar{c}^2,$$

where m is the mass of a molecule; and if $\bar{E}$ is the mean molecular kinetic energy, then—

$$\bar{E} = \frac{1}{2}m\bar{c}^2.$$

Hence

$$p = \frac{1}{3}nm\bar{c}^2 = \frac{2}{3}n\bar{E},$$

where n is the number of molecules per c.c.

The experimental gas laws are summarised in the statement that—

$$pv = RT,$$

where v c.c. is the volume of one gram-molecule of the gas under the pressure p at the temperature T and R is the gram-molecular gas constant.

Hence we derive—

$$\frac{2}{3}nv\bar{E} = RT, \text{ or } \bar{E} = \frac{3}{2} \cdot \frac{R}{nv} \cdot T.$$

But nv is the number of molecules in the gram-molecule; so R/nv is the gas constant per molecule, usually denoted by k . Thus we obtain, as the connection between the temperature of the gas and its mean molecular motion—

$$\bar{E} = \frac{3}{2}kT \quad (8)$$

We have so far dealt with a gas composed of similar molecules, but if we consider a gas mixture containing molecules of different masses, little alteration is required in the formulæ. It can be shown that among each group of molecules of one type, the relative distribution in speed and direction is similar to that already outlined for a simple gas, and is unaffected by the presence of other types of molecules. This is a statistical generalisation of the well-known law of Dalton concerning gas mixtures. Thus, each group of molecules has a certain r-m-s-speed, but the value of this varies from group to group; however, a very simple relation connects them. If we denote types of molecules by suffixes, 1, 2, 3, etc., then—

$$m_1\bar{c}_1^2 = m_2\bar{c}_2^2 = m_3\bar{c}_3^2 = \text{etc.}$$

where m_1, m_2, m_3 , etc., are the masses of each type of molecule. In terms of average kinetic energies per group of molecules this is—

$$\bar{E}_1 = \bar{E}_2 = \bar{E}_3 \quad \text{etc.}$$

Referring to (8) we see that this dynamical conclusion is the statistical statement of the equality of temperature which obtains throughout the gas mixture when a steady state has been attained. On account of this relation it becomes more convenient to state the distribution law in terms of limits of kinetic energy. This is easily done. Thus, reverting to the case of a simple gas for a moment, we introduce the following changes into (4):—

Write

$$\begin{aligned} E &= \frac{1}{2}mc^2 \\ \bar{E} &= \frac{1}{2}m\bar{c}^2 \\ dE &= mc \cdot dc \end{aligned}$$

and we obtain after a few steps—

$$4\pi N \sqrt{\frac{27}{32\pi^3 \bar{E}^3}} \cdot E^{\frac{1}{2}} \cdot e^{-3E/2\bar{E}} dE$$

as the number of molecules with kinetic energies between E and $E + dE$ at an instant.

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We may avail ourselves of (8) and obtain instead of this expression the following one:—

$$\frac{2N}{\sqrt{\pi k^3 T^3}} \cdot E^{\frac{1}{2}} \cdot e^{-E/kT} \cdot dE \quad (9)$$

as the number of molecules limited in the manner mentioned.

Now it can be shown that for a gas mixture consisting of N_1 molecules of type 1, N_2 molecules of type 2, etc., in a steady state, and therefore with the same mean energy of motion (*i.e.* the same temperature) throughout, the number of molecules of type 1, of type 2, etc., within the defined limits of kinetic energy are given by expression (9), with N replaced by N_1, N_2 , etc., in succession. Briefly, the distribution of kinetic energy ignores differences in molecular mass.

Hitherto we have considered the gas to be free from all external forces such as gravity, and subject only to the forces arising from collision with each other or with the comparatively fixed molecules in the solid walls of the containing vessel. If we introduce external forces of a conservative type the previous formulæ must be modified as follows:—

Denote the co-ordinates of a point in the gas as X, Y, Z ; the potential energy of a molecule m of the gas at this point is a function of X, Y, Z ; call it χ_{XYZ} or simply χ .

We no longer have a uniform density of distribution in *position* for the molecules. The density, in fact, diminishes as we move to places of greater potential energy. A good illustration of this is the progressive decrease in the density of the atmosphere as the altitude increases. It can be shown that the molecular density is proportional to—

$$e^{-\chi/kT}.$$

Hence, the number of molecules in an element of volume dx, dy, dz at the point XYZ is—

$$ne^{-\chi/kT} dx dy dz,$$

where n is a constant. As a matter of fact n is the molecular density in a small volume surrounding a point where the potential energy, χ , is zero.

The distribution in kinetic energy of the molecules in this element of volume is just as before. Hence we can write in full—

$$\frac{2n}{\sqrt{\pi k^3 T^3}} \cdot E^{\frac{1}{2}} e^{-(E+\chi)/kT} dE \cdot dx dy dz \quad (10)$$

as the number of molecules in an element of volume $dx dy dz$, where the potential energy of a molecule is χ , and whose kinetic energies lie between E and $E + dE$.

The extension of this result to the case of a gaseous mixture is easily given. Let the potential energies of each type of molecule in the external field of force at the point XYZ be χ_1, χ_2, χ_3 , etc.; then the

numbers of each type of molecule in the volume element $dx dy dz$, at this point limited as in (10), are—

$$\left. \begin{aligned} & \frac{2n_1}{\sqrt{\pi k^3 T^3}} \cdot E^{\frac{1}{2}} \cdot e^{-(E+\chi_1)/kT} dE dx dy dz \\ & \frac{2n_2}{\sqrt{\pi k^3 T^3}} \cdot E^{\frac{1}{2}} \cdot e^{-(E+\chi_2)/kT} dE dx dy dz \end{aligned} \right\} \quad (11)$$

and so on.

Here n_1, n_2 are the molecular densities of each type of molecule around a point where the potential energy is zero.

The formulæ developed hitherto have postulated implicitly an *absence* of intermolecular forces, except such as arise in a collision between molecules, an event which, though *absolutely* very frequent for a molecule, is *relatively* rare, since the time which a molecule spends in its free paths is very much larger than the time spent in collisions. When we introduce intermolecular forces, *i.e.* when we approach the liquid or solid state, the formulæ become more complex, and as they are not required in the text of the chapter to which this appendix refers, may be laid aside.

A more important case for our purpose is the case of a gas whose molecules can no longer be considered as simple rigid bodies, but for which an atomic and even a sub-atomic structure must be postulated. It would take us too far afield to treat the formulæ for this case in all their generality, but we can deal with a few statements of service later.

As before, we take the number of molecules as N , and consider that the general position of each molecule is given by the three Cartesian co-ordinates of its centre of mass. Besides these three co-ordinates there are other geometrical quantities (or co-ordinates in a more general sense) necessary to define the structure of a molecule. These *internal* co-ordinates can be most readily thought of as the *least* number of lengths and angles necessary to specify the position of every distinct and conceivably separate part of the molecule with regard to its centre of mass. The number of these co-ordinates constitute the internal "degrees of freedom" of the molecule. Suppose there are n of them, the necessary n co-ordinates being denoted by the letters—

$$q_1 q_2 \dots q_n$$

The rates of change of these co-ordinates as the molecular parts move relatively to one another are referred to as "components of velocity" or simply "velocities," each corresponding to a definite degree of freedom. Writing $\dot{q}$ for dq/dt , these velocities are—

$$\dot{q}_1 \dot{q}_2 \dots \dot{q}_n$$

As the parts of the molecule act on each other by means of inter-atomic and intra-atomic forces (of electric origin), the molecule possesses a certain amount of internal potential energy, as well as a certain amount of internal kinetic energy due to the motions of the parts rela-

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tive to the centre of the mass. This kinetic energy can be expressed as a quadratic function of the velocities $\dot{q}_1, \dots, \dot{q}_n$. The case which has been most extensively treated, and which is very amenable to mathematical analysis, permits of the potential energy also being expressed as a quadratic function of the co-ordinates $q_1, \dots, q_n$. This assumption is possible when we have to deal with the *small* oscillations of the various parts about positions of relative equilibrium, or about states of steady relative motion, and these conditions have thrown a great deal of light, e.g. on the radiating mechanisms of molecules. It is possible with this assumption so to choose the co-ordinates that the total internal energy, kinetic *and* potential, involves only squares of the co-ordinates and velocities, so that we can write the *total* internal energy ϵ as—

$$\epsilon = a_1 \dot{q}_1^2 + \dots + a_n \dot{q}_n^2 + b_1 q_1^2 + \dots + b_n q_n^2,$$

where $a_1, \dots, a_n, b_1, \dots, b_n$ are constants.

In this manner and under the conditions laid down we can, as it were, partition the energy among the various degrees of freedom, $a_1 \dot{q}_1^2$ being, for example, the kinetic energy “belonging to” the first degree of freedom, and $b_1 q_1^2$ the potential energy belonging to the same degree of freedom, and so on. There is in addition, of course, the kinetic energy of translation of the molecule as a whole, *viz.* $\frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\dot{z}^2$, which we will write as K involving three more degrees of freedom, with the energy as before partitioned between the three degrees.

We can now state some results of the application of statistical mechanics to a system of such molecules. It must be understood, however, that these results rest on the validity of the classical dynamics. Of late these results have been impugned by Planck and others, and the foundations of dynamics are undergoing a revision. It will, however, enable the reader to grasp the modifications proposed if he masters the following few statements and accepts their truth at all events provisionally.

As the molecule moves about and its parts oscillate with regard to each other, its energy changes, not only *in toto* but also in its several terms. It can be shown, however, that the mean energy, kinetic *or* potential, belonging to any co-ordinate, averaged over a considerable period of the molecule's history, is the same for all the degrees of freedom and is equal to $\frac{1}{2}kT$. That is—

$$\overline{\frac{1}{2}m\dot{x}^2} = \overline{\frac{1}{2}m\dot{y}^2} = \overline{\frac{1}{2}m\dot{z}^2} = a_1 \overline{q_1^2} = a_2 \overline{q_2^2} = \dots = b_1 \overline{q_1^2} = b_2 \overline{q_2^2} = \dots = \frac{1}{2}kT.$$

This is a statement of the famous theorem due to Maxwell and usually referred to as the “equipartition of the energy among the various degrees of freedom.”

Further, it can be shown, as before, that the number of molecules which have velocities between uvw (*i.e.* $\dot{x}\dot{y}\dot{z}$) and $u + du, v + dv, w + dw$ is—

$$A N e^{-\kappa/kT} du dv dw \quad (12)$$

where A is a constant.

Of this limited number a still more limited number exists at one instant whose several total internal energies, kinetic *and* potential, lie between ϵ and $\epsilon + d\epsilon$.

This latter number forms a fraction of the former whose value is—

$$B\epsilon^n = 1e^{-\epsilon/kT}d\epsilon \quad . \quad . \quad . \quad . \quad (13)$$

where B is a constant.

Combining the two expressions, we have the number whose internal energies lie between ϵ and $\epsilon + d\epsilon$, and whose general velocities of translation lie between uvw and $u + du, v + dv, w + dw$, as—

$$C \cdot N \cdot \epsilon^n = 1 \cdot e^{-(\epsilon + 1/2kT)/kT} d\epsilon du dv dw \quad . \quad . \quad . \quad . \quad (14)$$

where C is a constant.

As an important particular case, expression (13) reduces for one *internal* degree of freedom to—

$$B\epsilon = 1e^{-\epsilon/kT}d\epsilon \quad . \quad . \quad . \quad . \quad (15)$$

Equation (15) forms the basis of the expression of Marcelin and Rice for the rate of decomposition of a molecule referred to in Chapter VII. under the heading “Reaction velocity from the standpoint of the quantum theory”. The expression for the velocity constant on the basis of statistical mechanics is given by Rice (*Brit. Ass. Report*, 1915, p. 397, and *Phil. Mag.*, 1923).

APPENDIX II.

FOUNDATIONS OF THE QUANTUM THEORY.

By J. RICE, M.A.

(From the *Transactions of the Faraday Society*, xi., p. 1, 1915.)

DURING the nineteenth century certain facts had been well established concerning the radiation contained in an enclosure maintained at constant temperature. Balfour Stewart and Kirchhoff had shown that if the material of the walls was not perfectly reflecting for any quality of radiation, any constituent of the radiation having a definite frequency was present in an amount depending on that frequency, the temperature and size of the enclosure, but independent of the nature of the wall-material. Stefan and Boltzmann had proved that the energy of the total radiation in one c.c. was proportional to the fourth power of the absolute temperature. Wien had reached the conclusion that the energy-density of those constituents of the radiation, whose wave-lengths

lay between narrow limits λ and $\lambda + \delta\lambda$, was $\frac{f(\lambda T)}{\lambda^5} \delta\lambda$, where the function f in the numerator, although undetermined in form, was dependent on the single variable λT , the product of the wave-length and the absolute temperature. These statements had been arrived at by reasoning of a purely thermodynamic nature, based on the existence of a radiation pressure. It was only natural that the statistical methods, already employed as a successful weapon of attack on problems arising out of the kinetic theory of gases, should be presently pressed into service in this new line of research. There is some resemblance between a vessel containing molecules, individually uncontrollable but maintaining a certain average condition of energy by encounters, and an enclosure maintaining a statistically permanent condition of radiation by the emission and absorption of its walls, while the history of any particular wave-train of definite frequency cannot be followed in detail. There is one marked difference between the two cases: molecules can, by direct encounter with each other, as well as by collision with the walls, exchange energy; but in a temperature enclosure passage of energy from one wave-train to another must take place through the agency of the walls alone or of matter contained within them, since two such trains can pass through the same element of volume (*i.e.* cross one another without any change in the energy or quality of the trains). For

this reason, if the walls are perfectly reflecting, any arbitrary condition of radiation supposed existing at one moment would remain permanently unaffected in the energy and quality of its constituents, and only by the introduction of a piece of non-reflecting matter into the enclosure could the radiation be gradually brought to the condition of "full" or "complete" radiation for the temperature, the condition considered by Balfour Stewart and Kirchhoff.

Wien, himself, had made an attempt to determine the form of the function in the numerator of his so-called displacement formula.¹ He considered the enclosure to contain a perfectly absorbing or "black" body, which he assumed to be a gas with its molecules distributed according to the Maxwell Law, and its temperature therefore proportional to the mean-squared velocity. A further hypothesis (a very doubtful one) was the assumption that those molecules whose velocities lie within certain narrow limits at a definite instant are at that instant emitting light within narrow frequency limits, with an intensity proportional to the number of those molecules. By these means Wien arrived at the

form $e^{-c/\lambda T}$ for his function $f(\lambda T)$, c being a constant. Measurements carried out shortly after by Lummer and Pringsheim, Beckmann, and Rubens verified the formula as a good representation of the facts for short wave-lengths, but found it completely at variance with the facts for long wave-lengths.

It was by the application of statistical principles in another direction that the next advance towards a correct radiation formula was made. Wien had considered the molecules of the black body. Lord Rayleigh, and afterwards Jeans, considered the radiation itself, assigned co-ordinates to it and "degrees of freedom," and applied the results of Maxwell's distribution law directly to these concepts. Such applications are certainly rather easier to apprehend "physically" in the case of gas molecules than in that of constituent wave-trains of radiation; there is more "substantiality" about a molecule than a wave-train. The representation of a molecule as a small, hard sphere with perfect resilience, which is quite adequate for many purposes, and analogies with billiard-balls, discs, etc., put one on fairly familiar terms with molecular motion and exchange of energy. The degrees of freedom of such simple systems are easily calculable, being in fact six for a "rigid" molecule of any shape. Even if we introduce atomic structure into the molecules, the degrees can still be computed if one knows the parts and their connections. The energy of the system at a given temperature is then obtained by the principle of equipartition, which is derived from the law of distribution, and asserts that the kinetic energy can be calculated by assigning to each degree of freedom an amount $\frac{1}{2}kT$ ergs, where k is the molecular gas constant (1.35×10^{-16} ergs/degrees), an equal amount of potential energy being also assigned to any degree of freedom, if there are "elastic" forces of the usual simple harmonic type.

¹ *Wied. Ann.*, 58, p. 662, 1896.

If such ideas are to be generalised and extended to the ether of an enclosure, a definite notion as to the structure of the ether is imperative before any headway can be made in calculating its degrees of freedom. At the outset it is fairly evident that the usual conception of the ether as a perfectly continuous medium indivisible into an enumerable number of discrete parts, should lead to an infinite number of degrees of freedom, with the resulting conclusion that in a state of equilibrium the ether in the enclosure should contain all the energy and the walls none. The well-known illustration of the gradual loss of vibratory energy from the particles of a sounding body to the surrounding air may serve to make this point clearer. This conclusion is in fact reached by the Rayleigh-Jeans analysis, and is very much at variance with the facts as we know them. The formula arrived at, however, is a close approximation to the truth for long wave-lengths, and the calculation of the number of degrees of freedom has proved of signal service in itself. It is impossible to reproduce the analysis here, but an analogy from sound waves may serve to show the principles on which it is based. It is well known that an organ-pipe will resound only to notes of definite frequencies, the fundamental and its overtones. This is due to the fact that any state of "stationary" wave-motion which will persist in the air of the pipe has to satisfy certain end conditions—e.g. at a closed end there can be no vibratory motion of the air particles, at an open end no change of pressure. Any text-book on sound shows that from these conditions there can exist in a very narrow pipe, closed at both ends or open at both ends, only waves whose wave-lengths are $2l$, $\frac{2l}{2}$, $\frac{2l}{3}$. . . $\frac{2l}{n}$, etc., where l is the length of the pipe. The frequencies are, of course, $\frac{v}{2l}$, $2\frac{v}{2l}$, $3\frac{v}{2l}$. . . $n\frac{v}{2l}$ etc., where v is the velocity of sound. Now if we write ν for $n\frac{v}{2l}$ we see that the number of possible modes of vibration whose frequencies are not greater than ν is $n = \frac{2l}{v} \cdot \nu$. Remembering that this is the result for a narrow pipe in which the wave-motion is parallel to one direction, let us extend the method to a flat shallow box, enclosed between two square ends so that the wave-motion takes place in any direction lying in one of the ends. The number of modes of vibration having ν as the upper limit of their frequencies would now be proportional to $\left(\frac{2l}{v} \cdot \nu\right)^2$, a result not difficult to apprehend, since we can in a rough sort of way suppose that with any one type of wave-motion parallel to one edge of the flat ends, we can compound any of the types which can exist parallel to the rectangular edges so as to obtain a possible wave-train travelling obliquely round and round the box, reflected continuously from the narrow long faces which also bound the box. If we still further extend these considerations to a cubical box, the number

of possible modes come out to be proportional to $\left(\frac{2l}{v} \cdot v\right)^3$, i.e. to $8\frac{\tau}{v^3} \cdot v^3$, τ is the volume of the box. A differentiation shows that the number of possible modes which lie between narrow limits of frequency ν and $\nu + \delta\nu$, is $24\frac{\tau}{v^3} \cdot \nu^2\delta\nu$. As a matter of fact a complete analysis shows that the numerical factor should be 4π and not 24. Now the point of this analogy lies in the fact that whatever be the nature of a beam of radiant energy, a certain definite condition has to be obeyed at a perfectly reflecting surface—on the electro-magnetic theory the tangential component of the electric intensity in the wave must be zero there—and this condition limits the number of types of radiation wave-trains which can persist unchanged as stationary waves in an enclosure with reflecting walls. Consequently, if we introduce a small portion of perfectly absorbing matter into a cube with perfectly reflecting walls, we can assert that, despite the fact that the matter can radiate and absorb any type of radiation, only those types will exist in the final state of equilibrium which satisfy the boundary conditions referred to above, just as our box organ-pipe would not resound to every small whistle introduced into it, but only to a whistle having one of a definite series of pitches. These types of radiation will constitute complete radiation at the temperature, since experiment has certainly justified Kirchhoff's conclusion that the frequencies and energies of the constituents of radiation in a temperature enclosure are independent of the size or nature or shape of the walls, so long as there is present a portion of non-perfectly reflecting matter. The number of types of radiation, therefore, which exist in full radiation, having frequencies between the narrow limits ν and $\nu + \delta\nu$, would appear to be $4\pi\frac{\tau}{c^3} \cdot \nu^2\delta\nu$, where c is the velocity of light; but, as a matter of fact, this number has to be doubled, since radiation waves are transverse to the direction of propagation (not longitudinal to it, as in the case of sound waves), and therefore any particular wave has to be regarded as due to the composition of two waves of the same period and phase, each polarised in one of two definite rectangular planes. So the final result for the number is $\frac{8\pi\tau}{c^3} \nu^2\delta\nu$. This means that in order to specify the electro-magnetic condition (electric and magnetic intensities) at any assigned point in the ether of the box, at any assigned instant, expressions involving a number $\frac{8\pi\tau}{c^3} \nu^2\delta\nu$ of terms each varying harmonically with the time would be required to designate that part of the effect due to waves of frequencies in the range $\nu, \nu + \delta\nu$. This number is in fact the number of independent co-ordinates or degrees of freedom for such qualities of radiation. Ascribing the usual KT units of kinetic and potential energy to each degree, we obtain for the energy of radiation in the range $\nu, \nu + \delta\nu$, the amount $\frac{8\pi\tau}{c^3} KT\nu^2 \cdot \delta\nu$ ergs, or for the energy-density,

$\frac{8\pi}{3}kTv^2 \cdot \delta v$ ergs per c.c. In terms of wave-lengths we obtain by putting $v = \frac{c}{\lambda}$ and $\delta v = -\frac{c}{\lambda^2}\delta\lambda$, that the energy-density of radiation whose wave-lengths lie in the range $\lambda, \lambda + \delta\lambda$ is $\frac{8\pi kT}{\lambda^4}\delta\lambda$ ergs per c.c.¹

It is an obvious drawback to the Rayleigh-Jeans expression that it does not approach a finite limit, as λ decreases to zero. In fact, the ether would appear to contain an infinite amount of energy per c.c. since—

$$\int_0^\infty \frac{d\lambda}{\lambda^4}$$

is certainly infinite.

We might evade this objection by observing that exchange of energy from one type to another must be effected by the material of the enclosure (as was pointed out above), and that we might reasonably suppose the radiating mechanisms in the atoms to be of such a nature that they could not emit radiation of a quality higher than a certain limiting frequency, and so the upper limit of the integral would be a finite quantity and not zero. But this would not meet the difficulty that for the same amount of range in wave-lengths $\delta\lambda$, there is a greater contribution to the energy density from high-grade qualities than from low-grade, according to the Rayleigh-Jeans formula; whereas experiment shows that the factor of $\delta\lambda$ exhibits a maximum value for a certain wave-length λ_m (dependent on temperature), and approaches zero as a limit as λ approaches zero or infinity.

It has been suggested that the tendency, expressed in the Rayleigh-Jeans Law, of the radiation energy to pass more and more into the higher qualities, is in reality a true phenomenon of nature, and that we fail to appreciate it in our experimental tests because all temperature enclosures fail to confine the energy of the highest frequencies; such energy leaks out, as it were, through the walls and through the small opening facing the radiometer, almost as fast as it is supplied from low-frequency radiation by the agency of the walls; and so the condition we actually observe is a compromise—a stage on the way to the final consummation expressed in the ideal formula, but unattainable except after an enormous lapse of time. The difficulty of accepting this suggestion is the difficulty of believing that such a compromise should be found to be so completely independent of the nature of the walls as experiment demonstrates. The formula, however, does agree with fact very well for long wave-lengths, just as Wien's does for short.

Faced with this discrepancy, there are two alternatives which offer themselves as obvious methods of escape from it. We may deny the

¹ *Phil. Mag.*, 49, 539, 1900; 10, 91, 1905; 17, 229, 1909. *Nature*, 72, p. 94 and p. 243, 1905.

validity of the calculation of the degrees of freedom, or we may urge objections to the law of equipartition of the energy. As a matter of fact, Planck's quantum hypothesis arises from his adoption of the second alternative, and a denial of the validity of equipartition in the case of vibratory motion. The principle of equipartition was first deduced in connection with the kinetic theory of gases. Now even in this original and limited sphere the principle does not stand on absolutely undebatable foundations. A great deal depends on the interpretation of the meaning to be attributed to the word "average". It is usually assumed that the average condition, say, of a molecule, is a "time" average, the sum of successive values of a quantity connected with the molecule, over a long period of change in the system, divided by the number of such values.

But it is doubtful if the principle of equipartition based on such an interpretation of the word "average" is really proved at all by dynamical principles. The point is fully treated by Jeans in his *Dynamical Theory of Gases*. It would appear that the "average" really referred to is an average extended over all conceivable conditions or "complexions" of a system (excepting a negligible number) and not merely over such conditions or "complexions" through which the system passes on any particular "path". The extension to "time" average cannot be made unless by the introduction of Maxwell's assumption of "continuity of path," viz. that the system will in process of time pass through all conceivable "complexions". This assumption is of doubtful validity, and is known to be unsound in certain of the problems treated in general dynamics, e.g. the periodic orbits of astronomy (a type of vibratory motion).

To proceed, Planck, denying the applicability of equipartition to radiation theory, works out from special considerations (to be dealt with presently) that in the vibratory motion obtaining in wave-trains, each degree of freedom corresponding to a frequency ν should possess on the average not kT ergs of kinetic and potential energy, but an amount—

$$\frac{h\nu}{e^{kT} - 1} \text{ ergs}$$

(where h is a new universal constant, determined by experiment to be approximately 6.55×10^{-27}). If we make use of the Rayleigh-Jeans calculation of the degrees of freedom, we find that the energy density of the radiation in the range $\nu, \nu + \delta\nu$ is—

$$\frac{8\pi}{c^3} \frac{h\nu^3}{e^{kT} - 1} \cdot \delta\nu \text{ ergs per c.c.,}$$

or in terms of wave-lengths—

$$\frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{k\lambda T} - 1} \cdot \delta\lambda \text{ ergs per c.c.}$$

These expressions agree remarkably well with the most recent measurements for all values of ν or λ , enabling the calculation of h to be made with some precision.¹

It is only natural that, in adopting a more or less revolutionary attitude to a principle hitherto enjoying the confidence of the scientific world, Planck and his followers should have modified somewhat the original presentation of their ideas to meet the various criticisms urged by those who seek to retain the traditional standpoint. It is well known that Planck himself has receded somewhat from the position adopted in his earlier papers on the subject. This position is fully expounded in the first (1906) edition of his book, *Theorie der Wärmestrahlung* (Leipzig, Barth); the latter form of his theory is contained in *Deutsch. Phys. Gesell. Ver.*, **13**, 3, 138, 1911, or in the second (1913) edition of the above book. Einstein's speculations and applications are to be found in various papers in the *Annalen der Physik* from 1905 onwards.

It is impossible to reproduce the whole of Planck's line of argument here, but the following brief account will bring out the essentially novel principle introduced by him, and serve also to show to some extent why and how he receded from the earlier to the later position.

He remarks that any radiating mechanism of frequency ν , placed in a temperature enclosure, will acquire an average energy depending on the energy-density of the radiation of that frequency in the enclosure. The radiating mechanism of which he avails himself is an electric doublet, consisting of an electrified particle vibrating harmonically under the attraction of an oppositely electrified nucleus to which it is held by a force of the usual elastic, proportional-to-the-displacement type. In the enclosure there exist a great number N of these doublets or "oscillators," having their axis fixed in a certain direction, *i.e.* endowed with one degree of freedom. By an application of the usual equations of the electro-magnetic field, he shows that—

$$U(\nu) = \frac{8\pi\nu}{c^3} L(\nu) \quad (1)$$

where $L(\nu)$ is the mean energy (kinetic and potential) of an oscillator and $U(\nu) \cdot \delta\nu$ is the energy-density of the radiation in range ν to $\nu + \delta\nu$. Of course if we put $L(\nu)$ equal to kT , as usual, we would arrive as before at the Rayleigh-Jeans Law. Planck, however, avoids this by assuming that his oscillators can only emit and absorb discontinuously, and that at any instant the energy of an oscillator can only be an integral multiple of a finite unit or "quantum" of energy, the amount of the unit depending on the frequency. It is to be carefully noted that this does not imply, of necessity, an atomic structure for energy—a view, indeed, repudiated by Planck; it does imply that the oscillator must emit or absorb whole quanta of radiation at one time (at present, be it noted, we are discussing Planck's earlier views). Now such an

¹ *La Théorie du Rayonnement* (Gauthier-Villars, 1912), pp. 78-92.

assumption necessarily involves a modification of Maxwell's distribution law, for that law depends on the possibility of the infinite divisibility of the energy among the oscillators, atoms, molecules, and so forth. The point is more easily followed with aid of a "condition-diagram". Suppose we denote the charges of the doublets as $\pm e$, the mass of the vibrating particle as m , and x as its displacement along its axis at time t , then the equation of its "free" motion is—

$$\ddot{x} + 4\pi^2\nu^2 \cdot x = 0$$

or

$$m\ddot{x} + 4\pi^2\nu^2 \cdot mx = 0,$$

where ν is the frequency. If X is the resolved component of the electric intensity of the field along x at time t , the equation of its forced motion is—

$$m\ddot{x} + 4\pi^2\nu^2 mx = eX \quad (2)$$

If we denote the energy of the particle by ϵ —

$$m\dot{x}^2 + 4\pi^2\nu^2 mx^2 = 2\epsilon,$$

or denoting its momentum by $y (= m\dot{x})$ —

$$y^2 + 4\pi^2\nu^2 m \cdot x^2 = 2\epsilon \quad (3)$$

Now the condition of any oscillator as regards the displacement and momentum of its vibrating particle can be clearly represented on a plane diagram by a point with co-ordinates x and y . All those oscillators whose energy is ϵ have their representative points lying on the ellipse—

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1,$$

where

$$2\pi^2\nu^2 \cdot m'$$

and

$$b^2 = 2\epsilon m.$$

The area of this ellipse is of course πab , i.e. $\frac{\epsilon}{\nu}$.

The history of any oscillator can be represented by the motion of a point on this diagram, travelling along a curve, passing outward from the origin when the energy of the oscillator is increasing, and inwards when the energy is decreasing. Maxwell's Law states that the number of oscillators whose displacements and momenta lie between the limits x, y , and $x + \delta x, y + \delta y$ is—

$$A \cdot e^{-\frac{\epsilon}{kT}} dx dy \quad (A \text{ being a constant}).$$

If we integrate this over the narrow ring in the diagram between two ellipses determined by values of the energy ϵ and $\epsilon + \delta\epsilon$, we have

for the number of oscillators whose energies lie between ϵ and $\epsilon + \delta\epsilon$, the expression—

$$Ae^{-k\tau\delta\epsilon/\nu}.$$

Of course, on the assumption of infinite divisibility of the energy, the total number of oscillators, N , should be—

$$A \int_0^\infty e^{-k\tau\epsilon/\nu} d\epsilon.$$

But the essence of Planck's idea is that this integral should be replaced by a convergent series. For, according to his ideas, the representative points can only be found on the ellipses corresponding to energies $\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_n$, etc., where ϵ_1 is the quantum of energy and $\epsilon_n = n \cdot \epsilon_1$; they will lie nowhere between these ellipses. The points will, as it were, jump from ellipse to ellipse. The areas of these ellipses are of course—

$$\frac{\epsilon_1}{\nu}, \frac{\epsilon_2}{\nu}, \frac{\epsilon_3}{\nu}, \text{ etc., or } \frac{\epsilon_1}{\nu}, 2\frac{\epsilon_1}{\nu}, 3\frac{\epsilon_1}{\nu}, \text{ etc.,}$$

and the various rings between them have all a common area. It is a feature of Planck's theory that he gives this area a constant value for all oscillators of any period, and denotes it by the letter " h ," so that—

$$\begin{aligned}\epsilon_1 &= h\nu, \\ \epsilon_2 &= 2h\nu, \\ \epsilon_3 &= 3h\nu, \text{ etc.}\end{aligned}$$

The integral expression N above must now be replaced by the series—

$$\begin{aligned}N &= \frac{A}{\nu} \left[e^{-0} \cdot \epsilon_1 + e^{-k\tau(\epsilon_2 - \epsilon_1)} + e^{-k\tau(\epsilon_3 - \epsilon_2)} + \text{etc.} \right] \\ &= \frac{A}{\nu} \left[h\nu + e^{-k\tau h\nu} + e^{-k\tau 2h\nu} + \dots \right] \\ &= Ah \left[1 + e^{-k\tau h\nu} + e^{-k\tau 2h\nu} + \dots \right] \\ &= Ah \frac{1}{1 - e^{-k\tau h\nu}} \dots \dots \dots (4)\end{aligned}$$

If we now wish to calculate the total energy E , we see that the oscillators corresponding to the first term of the above series have no energy, those corresponding to the second have each $h\nu$, those to the third have each $2h\nu$, and so on. Hence we have—

$$\begin{aligned}& Ah \left[e^{-\frac{h\nu}{k\tau}} h\nu + e^{-\frac{2h\nu}{k\tau}} 2h\nu + e^{-\frac{3h\nu}{k\tau}} 3h\nu + \dots \right] \\ & Ah^2 \nu e^{-\frac{h\nu}{k\tau}} \left[1 + 2e^{-\frac{h\nu}{k\tau}} + 3e^{-\frac{2h\nu}{k\tau}} + \dots \right]\end{aligned}$$

$$\begin{aligned}
 &= e^{-\frac{h\nu}{kT}} \frac{A h^2 \nu}{\left(1 - e^{-\frac{h\nu}{kT}}\right)^2} \\
 &\quad \frac{N h \nu \cdot e^{-\frac{h\nu}{kT}}}{1 - e^{-\frac{h\nu}{kT}}} \\
 &= \frac{N h \nu}{e^{\frac{h\nu}{kT}} - 1} \quad (5)
 \end{aligned}$$

$$\therefore L(\nu) = \frac{E}{N} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \quad (6)$$

By equation (1) it follows that—

$$U(\nu) = \frac{8\pi}{c^3} \cdot \frac{h\nu^3}{e^{\frac{h\nu}{kT}} - 1} \quad (7)$$

an equation which agrees well with observed results, if, as has already been noted, h is put equal to 6.55×10^{-27} . It should be evident now that Planck escapes from the Rayleigh-Jeans conclusion entirely by his hypothesis of discontinuity in the exchanges of energy between the oscillators and the medium. Had he assumed that $\epsilon_1, \epsilon_2 = \epsilon_1, \epsilon_3 = \epsilon_2$, etc., are infinitesimally small, he would have found for $L(\nu)$ in (6) the limit of the right-hand expression as $h\nu$ approaches zero, which is just kT , and so have arrived back at equipartition and the previous discrepancy. His essential point is, in fact, the assumption that h is finite, *i.e.* that the “elementary region of the condition diagram” has a finite size. So that in a sense Planck’s theory is more an innovation in the method of probabilities, and need not be confined to radiation problems. This point will be touched on later.

Two obvious criticisms of this first line of argument have been advanced. First, equation (1) is obtained by an application of electromagnetic equations which rest on the assumption of a continuous exchange of energy between oscillators and medium. But as Campbell in his *Modern Electrical Theory* (2nd edition) points out, this may not be a fatal flaw in the reasoning. Maxwell’s equations may be quite true for average values of the electric and magnetic quantities involved without implying their absolute validity at all instants in the immediate neighbourhood of one oscillator, and so equation (1) might still stand as an equality of average values, even though the discontinuity assumed by Planck existed for individual doublets and their near environment. It should be noted, however, in passing, that at a high temperature, say 2000°C . the quantum of energy for high-grade light of the order $\nu = 10^{15}$ is 30 times as large as the average energy of an oscillator in these conditions.

The second objection is that to produce the enormously great

number of qualities which are known to exist in complete radiation, we should have to postulate the existence of a very great number of oscillators of different frequencies. Now, all the evidence which we possess on the nature of atomic structure negatives such a view, nor is there any real evidence that any vibrating electron in an atom emits simple harmonic waves at all. Indeed, one of the outstanding difficulties of the Planck theory is just this difficulty of formulating a plausible physical basis for it.

There is a further difficulty awaiting us when we seek to apply the notion of discontinuous absorption to the phenomena of ejection of electrons from the surfaces of bodies on which is incident a beam of ultra-violet light (the photo-electric effect), or a pencil of X-rays. All the evidence favours the view that a definite amount of energy has to be at least resident in the electron before it can be ejected. In the normal photo-electric effect the energy of the electron after escape is found to have a maximum value $h'\nu - w$, where ν is the frequency of the incident light, h' a constant whose value agrees fairly closely with Planck's h , and w is a constant characteristic of the metal from which the electrons are escaping. A quite plausible hypothesis is that $h'\nu$ represents the amount of energy in the electron before its escape; of this it loses an amount w in leaving the atom against restraining forces, which depend on the particular structure of the atom; and so, if it is on the surface and has not to part with still more energy in escaping from the influence of neighbouring atoms, it would retain an amount $h'\nu - w$ after emergence. Now this appears to fit very well indeed with Planck's original assumption of the discontinuous and sudden absorption of a quantum $h\nu$, which, if ν is large enough, would supply the necessary energy for the escape of the electron from those atoms which the laws of chance brought at any definite instant into the suitable condition for absorption. But there seems to be this fatal objection to such a simple hypothesis, that the photo-electric effect has been observed *without any delay* in cases where the intensity of the light, as calculated by the inverse square law and on the assumption of continuous propagation through the ether, could not have possibly supplied the necessary quantum to an electron in a molecule or atom in less than 10 or 15 minutes. Similar difficulties arise in connection with the secondary β -rays caused by X-rays, if one considers the energy of the X-ray pulse as uniformly distributed throughout the pulse. In fact, if one adheres to the hypothesis of discontinuous absorption, one must admit that the energy of any beam of radiation is not uniformly diffused throughout the space occupied by the beam. This is, indeed, roughly the manner in which Einstein escapes from the difficulties. He has advanced the view that the energy of light is itself atomic in structure, and absorption and emission are of necessity discontinuous, not because of the special structure of the oscillators, etc., but because of the nature of light itself. His view is, in reality, a quantum of energy view; it has already been observed that Planck's is not necessarily so; indeed, Planck dissociates himself at present from so revolutionary a hypothesis. It is noteworthy

that J. J. Thomson had already been led to speculations somewhat similar to Einstein's, by considerations based on his hypothesis of Faraday tubes in the ether emanating from charged particles.¹ It should be noted that Thomson's view of a "filamental" structure in the ether might well be expected to lead to a different result for energy-density than that reached by Rayleigh and Jeans; for their calculation of the degrees of freedom in the ether, it will be recalled, depends on taking the ether as a perfectly continuous medium. Such a view would indeed be more like the adoption of the first of the alternatives referred to previously as methods of escape from the Raleigh-Jeans discrepancy. In reference to such views, it must be admitted that, however useful they may be for the immediate purpose of overcoming such difficulties as those connected with the photo-electric effect, and X-rays, and however well they suit the needs of radiation formulæ, they involve a return to the corpuscular theory of light, a raising of all the old difficulties of accounting for diffraction and interference on such a theory, and at present they lack a system of fundamental postulates, such as those on which stands the present edifice of dynamics and electro-dynamics. Of course, there is no gainsaying that the construction of such a system may be attempted and may be successfully carried out, and Newtonian dynamics placed in the position of a good approximation to truth, but without absolute validity.

As has been already suggested, Planck meets these difficulties in a less revolutionary fashion; he abandons the hypothesis of discontinuous absorption, retaining discontinuous emission. By so doing he meets fairly successfully (though not entirely, as I hope to show presently) the objection lodged against his method of obtaining equation (1). His new hypothesis concerning his oscillators is that they can emit only at definite instants, *viz.* when they contain an integral number of quanta, $h\nu$. If they contain any fraction of a quantum over an integral number they cannot radiate. When radiation does take place it is "catastrophic," *i.e.* it cannot cease until the whole energy of the oscillator has been lost. The particular number of quanta possessed by an oscillator when it radiates are determined by the laws of chance, the chance of its reaching a given number being less the greater the number and the smaller the radiation-density. In fact, Planck's new line is based on three postulates:—

- (a) In any finite time the total emission equals the total absorption.
- (b) For small frequencies (*i.e.* long wave-lengths), the quanta of energy are so small that emission is practically continuous, and the ordinary dynamical and electro-dynamical laws are a good approximation to the facts even for individual oscillators and their immediate neighbourhood.
- (c) The chance of a particular oscillator emitting when arriving at a "critical" state (*i.e.* containing an integral number of quanta) is less the stronger the field. In particular, the chance of no emission taking

¹ *Electricity and Matter* (Constable, 1904). *Phil. Mag.*, 19, 301, 1910.

place to the chance of an emission is a ratio proportional to the radiation-density.

Concerning these (a) is clearly a statement of fact in a state of equilibrium; (b) is a justifiable hypothesis, inasmuch as the Rayleigh-Jeans formula is suitable for experiments on long wave-lengths. As regards (c), the first part of it is plausible enough, but the particular statement of it in the second sentence appears to be an *a posteriori* assumption, based on the necessity of arriving at a formula (already experimentally proven) by the method employed.

To proceed to a brief outline of his new analysis, Planck replaces equation (1) by another, giving the rate of absorption of an individual oscillator in a field of given radiation-density. With the same notation as before, he finds on the basis of equation (2) (taken to be valid for continuous absorption) that—

$$\frac{dI(\nu)}{dt} = \frac{\pi e^2}{3m} U(\nu) \quad (8)$$

As the right-hand expression is clearly positive, the equation refers to an increase of the oscillator energy, *i.e.* absorption.

Adopting the same geometrical representation of the condition of an oscillator as before, the history of an oscillator is not represented now by the leaping of a point from one to another of the "critical" ellipses corresponding to the energies. $h\nu$, $2h\nu$, $3h\nu$, etc. Its behaviour follows the continuous movement of a point from the origin outwards, and a jump back to the origin when the point reaches some one of the "critical" ellipses (the particular one being a matter of chance), the outward journey being once more resumed. The number of oscillators is as before given by—

$$N = Ah \int_0^\infty \frac{1}{e^{h\nu/kT}} \nu d\nu \quad (4)$$

but the equation (5) for E must be altered. The energy of any oscillator is no longer, at any instant, an integral number of quanta; all amounts can exist, and the average energy of an oscillator whose representative point is known to lie in a particular ring must be taken as the mean of the energies corresponding to the elliptical boundaries of the ring, *i.e.* it must be an integral number of quanta plus half a quantum. On this basis it is easy to show that (5) must be replaced by—

$$\frac{N h \nu}{e^{h\nu/kT} - 1} + \frac{N h \nu}{2} \quad (9)$$

and therefore

$$L(\nu) = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} \quad (10)$$

on the average.

Of course we cannot apply equation (1) to this; that has been discarded, and replaced by (8); but before proceeding further it may be

as well to remark that Planck's new hypothesis enables him to account for the photo-electric effect taking place without delay, even for weak light; for obviously there are at any instant a number of oscillators just within an infinitesimally small amount of energy from arrival in a "critical" state, and of these a portion will radiate almost instantaneously, or eject an electron. Thus Planck avoids Einstein's revolutionary postulate on the atomicity of energy.

We saw above that the number of oscillators whose energy lies between ϵ and $\epsilon + \delta\epsilon$ is—

$$Ae^{-\epsilon/kT} \delta\epsilon,$$

and so the number whose representative points lie between the n th and the $(n+1)$ th ellipse is $Ahe^{-(n+1)h\nu/kT}$; the number whose points are in the next ring are $Ahe^{-(n+2)h\nu/kT}$. That is, of all those which acquire an amount of energy between $n h\nu$ and $(n+1)h\nu$, the fraction $e^{-h\nu/kT}$ pass the $(n+1)$ th "critical" state and acquire an amount of energy between $(n+1)h\nu$ and $(n+2)h\nu$. So $e^{-h\nu/kT}$ is the chance of no emission taking place, and therefore $1 - e^{-h\nu/kT}$ is the chance that an emission will take place. By postulate (c) above, we have—

$$\frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} = \rho U(\nu),$$

where ρ is a constant to be determined, i.e.—

$$\rho U(\nu) = \frac{1}{e^{h\nu/kT} - 1} \quad (11)$$

therefore by equations (8) and (10)—

$$\begin{aligned} \rho h\nu \frac{dL(\nu)}{dt} &= \frac{\pi e^2}{3m} \frac{h\nu}{e^{h\nu/kT} - 1} \\ &= \frac{\pi e^2}{3m} \left(L(\nu) - \frac{h\nu}{2} \right) \end{aligned} \quad (12)$$

Now for small values of ν , $\frac{h\nu}{kT}$ is small and $L(\nu)$ approaches the value kT , $h\nu$ being therefore negligible in comparison with $L(\nu)$; so for *small values* of ν —

$$\rho h\nu \frac{dL(\nu)}{dt} = \frac{\pi e^2}{3m} L(\nu) \quad (12a)$$

Now Hertz has shown that in this case (for here by postulate (b) the classical methods are applicable) the rate of emission of a vibrating electric doublet is equal to the fraction $\frac{8\pi^2\nu^2e^2}{3c^3m}$ of its own energy.¹ But

in equilibrium the rate of emission is equal to rate of absorption, therefore Hertz's result gives us for our case—

$$\frac{dL(\nu)}{dt} = 8\pi^2\nu^2 e^2 \cdot L(\nu),$$

and so by

$$P/h\nu = 8\pi\nu^2$$

or

$$P = 8\pi h\nu^3$$

and therefore by (11) we obtain once more—

$$U(\nu) = \frac{8\pi}{c^3} \frac{h\nu^3}{e^{h\nu/kT} - 1}$$

Planck has thus succeeded in obtaining his radiation formula once more, but with the help of a rather artificial postulate (c), and also by ignoring the fact that his adoption of the electro-magnetic equations necessarily implies a continuous radiation from his vibrating electric particle. Such a particle in its excursions backwards and forwards along an ever-increasing amplitude must of necessity have a motion which is not uniform, but now accelerated, now retarded, and must during such variations of its motion be radiating; at least, that is the logical conclusion from traditional views. As a matter of fact, in a series of interesting papers in the *Phil. Mag.*, dealing with the line-spectra of the elements, Bohr frankly admits this point, but makes a most ingenious use of it, taking the first step in fact, towards a system of dynamics with which the behaviour of such systems as Planck's oscillators would harmonise.¹

It is doubtful if Planck's work would ever have received the consideration bestowed on it, had it not happened that an ingenious application of it by Einstein to the problem of specific heats initiated a remarkable series of researches, theoretical and experimental, which showed the hypothesis of discontinuity was fruitful of good results in other branches of physics and chemistry than radiation. It is well known that while high-grade radiation is exchanged by some mechanism which is sub-atomic in nature (vibrating electrons for instance), infra-red "heat" radiation is emitted and absorbed by means of the atoms and molecules as a whole. Einstein's idea was that in a monatomic *solid* each atom has a definite frequency of vibration, which, he assumed, can be determined by optical methods (the "residual ray" method of Rubens, for instance, or dispersion-formulae). If $L(\nu)$ is the expression used previously, each atom has on the average an amount of energy $L(\nu)$ for each degree of freedom, that is, $3L(\nu)$ altogether, on the basis of Planck's work, extending to "infra-red atom" oscillators.

¹ *Phil. Mag.*, July, September, November, 1913; March, 1914. Also cf. Chapter V.

Hence if there are N atoms per gram-atom in the body, the atomic heat of the body would be $3NL(\nu)$ or $\frac{3N_{2\nu}}{e^{h\nu/hT} - 1}$. A differentiation of this expression with respect to T would give the specific heat at the temperature T (for constant volume). The result is—

$$C = 3Nk \frac{x^2 e^x}{(e^x - 1)^2},$$

where $x = \frac{h\nu}{kT}$. If x is small, *i.e.* if ν is small or T large, this expression approaches the value $3Nk$, which is known to be 5.95 calories, and is indeed the Dulong-Petit value of the atomic specific heat. For small values of T , however, x is large and the above expression grows smaller and smaller, ultimately approaching the limit zero as T approaches zero or x approaches infinity. That is, there should be a gradual decrease to zero of the specific heat of a solid as the temperature approaches absolute zero. This was known to be true in a general way. Further, as C is a function of $\frac{\nu}{T}$, the curves connecting specific heat and temperature for various monatomic solids should be similar. In fact, for two solids whose atomic frequencies are ν_1 and ν_2 , the curve for the second would be obtained from the curve from the first by maintaining the same ordinates (representing C) and altering all the abscissæ (representing T) in the ratio $\nu_1 : \nu_2$. A series of now famous researches were undertaken by Nernst and his pupils: details of the work will be found in papers in the *Ann. der Phys.*, p. 395, 1911, in the *Zeitsch. für Electrochem.*, 1911 and 1912, in the *Théorie du Rayonnement*, and in Nernst's four lectures delivered at University College, London, on the solid state. The similarity of the curves was proved, while Einstein's actual expression, although following the general course of the change in specific heat with the temperature, exhibited considerable numerical discrepancies, especially at low temperatures. Nernst and Lindemann proposed an alternative formula—

$$C = 3Nk \frac{x^2 e^x}{(e^x - 1)^2} \left(\frac{1}{e^{2x} - 1} \right)^2$$

This, although in good agreement with results, was a piece of lucky guesswork, founded on no solid theoretical basis. In a paper in the *Ann. der Phys.*, 39, p. 789, 1912, Debye attacked the problem from a broad standpoint, and his result, from its agreement with experiment and the soundness of its premises, seems to have approached finality in this domain.

Debye points out that there can be no single "characteristic" vibration of the atoms of a monatomic solid. There are an enormous number of such vibrations; they constitute an "acoustic" spectrum;

they are the fundamental and overtones of the body considered as emitting a note. A knowledge of the elastic constants of the material is sufficient to determine them, just as Rayleigh and Jeans determined the frequencies possible in a cubical "block" of ether. For these vibrations constitute waves of "sound" travelling through the body with definite speeds. There are, for instance, "distortional" transverse waves travelling with a velocity v_1 , and "compressional" longitudinal waves travelling with a velocity v_2 . v_1 can be calculated if one knows the density ρ and modulus of rigidity μ of the material; it is in fact $v_1 = \sqrt{\frac{\mu}{\rho}}$; v_2 can be calculated if one knows in addition the bulk-modulus K —

$$v_2 = \sqrt{K + \frac{4\mu}{3\rho}}$$

Now, the number of degrees of freedom for vibrations having frequencies between ν and $\nu + \delta\nu$ is, as previously, $\frac{8\pi}{v_1^3}\nu^2\delta\nu$ per unit volume for the transverse waves, and $\frac{4\pi}{v_2^3}\nu^2\delta\nu$ for the longitudinal. (N.B.—The factor 8π occurs because the transverse waves are polarisable in two rectangular planes, the longitudinal are not.) Consequently the whole modes of vibration per unit volume between ν and $\nu + \delta\nu$ are $\left(\frac{8\pi}{v_1^3} + \frac{4\pi}{v_2^3}\right)\nu^2\delta\nu$. We saw above that the similar formula developed for the ether by Rayleigh and Jeans suffered from the drawback that, in integrating it, no finite upper limit could be assigned on account of the assumed continuity of the ethereal medium. In this case, however, there must be a finite upper limit to ν because the number of degrees of freedom cannot exceed $3N$ for a gram-atom of the substance.

Hence if ν_m is the highest frequency possible—

$$3N = \left(\frac{8\pi\tau}{v_1^3} + \frac{4\pi\tau}{v_2^3}\right) \int_0^{\nu_m} \nu^2 d\nu$$

(where τ is the volume of a gram-atom)

$$\begin{aligned} &= \left(\frac{8\pi\tau}{3v_1^3} + \frac{4\pi\tau}{3v_2^3}\right) \nu_m^3 \\ &= F\nu_m^3 \end{aligned}$$

where F is a constant, calculable from the elastic constants and density of the body.

Since $\nu_m = \left(\frac{3N}{F}\right)^{\frac{1}{3}}$ ν_m is also calculable. For Al, Cu, Zn, Ag, Pb,

Diamond it is of the order 10^{12} to 10^{13} . Now by ascribing, according to the extension of Planck's work, the energy—

$$\frac{h\nu}{e^{h\nu/kT} - 1}$$

to every degree of freedom, we obtain for the energy-content of body due to wave-motion of frequencies ν to $\nu + \delta\nu$ —

$$3V \cdot \frac{h\nu^3 \delta\nu}{e^{h\nu/kT} - 1},$$

or

$$\frac{9N}{\nu_m^3} \cdot \frac{h\nu^3 \delta\nu}{e^{h\nu/kT} - 1}.$$

Hence the total energy—

$$\begin{aligned} &= \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu^3 d\nu}{e^{h\nu/kT} - 1} \\ &= \frac{9NkT}{\alpha^3} \int_0^x \frac{y^3 dy}{e^y - 1} \end{aligned}$$

where

$$x = \frac{h\nu_m}{kT}, \text{ and } y = \frac{h\nu}{kT}.$$

A differentiation of this expression with regard to T produces this expression for the specific heat at constant volume—

$$C = 3Nk \left[\frac{12}{\alpha^3} \int_0^x \frac{y^3 dy}{e^y - 1} - \frac{3}{e^x - 1} \right]$$

This is clearly a function of x or $\frac{h\nu_m}{kT}$, and therefore suitably accounts for the similarity of the specific heat curves of different solids. Further, the expression agrees remarkably well with determinations of Nernst and his co-workers, more so in fact if ν_m is calculated not from the values of elastic constants, but from a formula discovered by Lindemann,¹ connecting ν_m and the melting point (taking ν_m as the frequency of vibration of an atom under the influence of its neighbours). The computation is not easily carried out, for the integral in the above expression cannot be evaluated in finite terms, and so one has to resort to the summation of series which can be obtained to suit various ranges of temperature as regards their convergency. One striking result emerges from the calculation, *viz.* that at very low temperatures the specific heat varies as the cube of the absolute temperature, this would appear to be true to within 1 per cent. for the range of temperature 0° to $\frac{h\nu_m}{12k}$.

Nernst has made a very happy combination of Einstein's and

¹ *Physikalische Zeitschrift*, **11**, 609 (1910).

Debye's formulæ in the treatment of diatomic solids such as KCl, NaCl, AgCl, KBr, and the triatomic substance PbCl₂. He supposes the heat content of the body to be constituted of two parts, one due to the vibrations of the molecules as a whole, and the other to the vibrations of the atoms within the molecules. The first part can be obtained by Debye's method, taking the upper limit of the frequency as determined by Lindemann's melting-point formula; the second part can be determined by Einstein's method, the characteristic frequency being determined by Rubens' "residual rays" method. The agreement with observation is quite good; details can be found in *Vortrage über die Kinetische Theorie der Materie und der Elektrizität* (Teubner). Still further extensions of Debye's ideas have been made by Born and Kármán and Thirring in papers contained in the *Phys. Zeit.*, 14 (1913).

It was pointed out above that Planck's formula is derived from an innovation in the treatment of statistical problems, the assumption, in fact, that the elementary region of the two-dimensional condition diagram for a system of oscillators is finite in area, and the replacement of Maxwell's integral by a series. Planck has applied the same idea to the six-dimensional condition diagram for an ideal monatomic gas, and arrived at a result which had been already obtained by Nernst, who bases his derivation of it on his well-known "heat theorem."¹ There are several ways of wording this theorem, according to the particular thermodynamic function which one elects to make use of in the statement. As expressed by Planck in his *Thermodynamics*, it is as follows: "The entropy of a condensed system, which is chemically homogeneous, is zero at the absolute zero of temperature." This law removes from the expression for the entropy of a body in a definite state that indefiniteness in value which arises in the usual thermodynamic treatment and which is due to the entrance into the formula of an undetermined constant on integrating the differential of the entropy. For clearly if the entropy of a body can be given definitely for one state, it is determinate for all other states which can be conceivably reached from the former by a reversible path. So if we can conceive that the body can be led to the condition of a chemically homogeneous solid or liquid at absolute zero, by a reversible process, Nernst's heat theorem makes it possible to calculate its entropy without ambiguity, if sufficient experimental data are available. By such means it can be shown that the entropy of one gram-molecule of an ideal gas is given by the equation—

$$S = C_p(1 + \log T) - R \log p + a \quad (13)$$

(absolute units of temperature, pressure, and energy being used), where the "chemical constant," a , indeterminate on pure thermodynamical grounds, has, according to Nernst's theorem, the value—

$$R \log \left(\frac{\theta^2}{p} \right) + \frac{5}{2} R \log \theta \quad (14)$$

¹ *Nachr. d. Ges. d. Wissensch. zur Göttingen Math. Phys. Kl.* (1906).

in which p_s is the vapour pressure of liquid condensed from the gas at a very low temperature, θ , and r_0 is the heat of vaporisation of the liquid at absolute zero.

Planck arrives at this result on dynamical grounds in the following manner. Conceiving a monatomic gas as an aggregate of particles with three effective degrees of freedom, and representing the co-ordinates of a particle by x, y, z , and its velocity components by u, v, w , the condition diagram is a six-dimensional one in which the position and momentum of a point representing a particle are given as x, y, z, mu, mv, mw (m being the mass of a molecule). According to the Maxwell Law the number of molecules whose representative points lie within the limits x, y, z, mu, mv, mw , and $x + dx, y + dy, z + dz, m(u + du), m(v + dv), m(w + dw)$ is—

$$N A e^{-\epsilon/kT} dx dy dz du dv dw \quad (15)$$

where N is number of molecules in a gram-molecule, ϵ the energy of a molecule in condition xyz, u, v, w , due to its position and velocity, and A is a number given by the equation—

$$A \int e^{-\epsilon/kT} dx dy dz du dv dw$$

If one puts $\epsilon = \frac{1}{2}m(u^2 + v^2 + w^2)$, it follows that—

$$A = \frac{1}{V} \left(\frac{m}{2\pi kT} \right)^{3/2}$$

V being the volume of the gas

Now, according to Planck's view, instead of the differential element of the six-dimensional diagram which occurs in (15), we ought to introduce a finite element having a value G , definite in size for a system of definite molecules. The form and position of these "elementary regions" would, as in the two-dimensional case, be bounded by the "surfaces" or loci of equal energy. If we number these regions 1, 2, 3, . . . n , we can say that a fraction f_1 of the representative points lie in region 1, etc., f_n in region n , where—

$$f_n = A \cdot e^{-\epsilon_n/kT} \cdot \frac{G}{m^3}$$

ϵ_n being the molecular energy corresponding to the n th region. With this notation, it is possible to express the entropy of the gas, as Boltzmann has shown (see his *Gastheorie*, or Jean's *Dynamical Theory of Gases*), in the form—

$$S = -kN \sum f_n \log f_n$$

Of course in Boltzmann's treatment, as in Maxwell's, f_1, f_2 , etc., are infinitesimally small, since the differential element $dx dy dz du dv dw$ occurs instead of $\frac{G}{m^3}$, and so the expression for S contains a constant

of indeterminate (and infinite) value. By assuming G to be finite, Planck avoids this conclusion, just as he avoids the Rayleigh-Jeans law in radiation, by assuming h to be finite and not infinitesimally small. He finds, by using the value given above for A and f_n , that—

$$S = kN \left[\log \frac{V(2\pi mkT)^{3/2}}{G} + \frac{E}{NkT} \right]$$

where E is the kinetic energy of the molecules

Writing R for kN and putting E equal to $\frac{3}{2}RT$, we obtain—

$$S = R \left[\frac{3}{2} (1 + \log V) + \log V + \frac{3}{2} \log (2\pi mk) - \log G \right] \quad (16)$$

Since $PV = RT$ and $c_p = \frac{5}{2}R$, equation (13) can be readily transformed to—

$$S = R \left[\frac{3}{2} (1 + \log P) + \log V - \log R + \frac{a}{R} + 1 \right] \quad (17)$$

The formal similarity between (16) and (17) is obvious, and the two results lead to the connection between Planck's G and Nernst's "chemical constant," a , given by the equation—

$$\frac{3}{2} \log (2\pi mk) - \log G = - \log R + \frac{a}{R} + 1,$$

or—

$$G = \frac{R(2\pi mk)^{3/2}}{e^{a/R + 1}}$$

The thermodynamic treatment can be found in the third edition of Planck's *Thermodynamics*, Chap. VI. The development of the ideas based on the quantum hypothesis is given in his *Theorie der Wärmestrahlung* (2nd edition, pp. 110-32).

APPENDIX III.

“PRESENT STATUS OF THE CONSTANTS AND VERIFICATION OF THE LAWS OF THERMAL RADIATION OF A UNIFORMLY HEATED ENCLOSURE.”

(Summary of a Paper with the above title by W. W. Coblentz, *Bur. Standards Scientific Paper*, No. 406 (1920)).

The two laws of radiation are:—

1. *The law of Total Radiation, i.e., the Stefan-Boltzmann law—*

$$R = \sigma(T_1^4 - T_0^4)$$

where R is the total emission of thermal radiation of all wave-lengths passing from a uniformly heated enclosure at a temperature T_1 to another body at a temperature T_0 . σ is the coefficient or constant of total radiation.

2. *The law of Spectral Radiation, i.e., the law which specifies the distribution of thermal emission intensities in the spectrum of the radiation emitted by a uniformly heated enclosure or so-called black body.* This law is best represented by Planck's formula—

$$E_\lambda = c_1 \cdot \lambda^{-5} (e^{c_2/\lambda T} - 1)^{-1}.$$

In this formula the constant $c_1 = 8 \cdot ch$, where c is the velocity of light *in vacuo*. The constant $c_2 = ch/k$ where k is the gas constant per molecule. c_2 may also be written as $4.9651 \times \lambda_{\max} \times T$ (Wien's Displacement Law). As is evident from the form of the equation, c_2 determines to a great extent the shape of the isothermal spectral energy curve.

The experimental investigations of thermal radiation consist essentially in determining whether σ and c_2 are constants, and the most probable numerical values of these quantities.

“The various methods are classified, and a brief description is given of each research. An attempt is made to indicate the good and the defective features of each research. This represents not only the writer's opinions but also those of other experimenters.

“It is shown that the great variation in the various determinations of the numerical values of the constants, especially the constant of total radiation, is owing mainly to the fact that, in the original papers, no corrections were made for atmospheric absorption of the radiation in its passage from the radiator to the receiver.

“In this paper conservative corrections for atmospheric absorption are applied to the various determinations to which such corrections had not been made. As a result, instead of wide variations in the various determinations, which are free from other obvious defects, there is a remarkably close agreement among the various numerical values. While it cannot be said that the true numerical values are exactly as here recorded, obviously the time is past when the value of the constants of radiation are swayed by a single and perhaps novel method of research.”

• THE COEFFICIENT OF TOTAL RADIATION (σ).

Observer.		Probable Value of $\sigma \times 10^5$.	Method
Kurlbaum .	1898	5.45	Bolometer
Féry .	1909	6.3	Thermometer
Bauer and	1909	5.3	Thermopile
Moulin }	1910	5.7	Pyrheliometer
Todd .	1909	5.48	Gas-conduction experiments
Valentine .	1910	5.58	Bolo meter
Féry and	1911	6.51	Ther nometer
Dreck }	1912	6.2	Pyro meter
Shakespear	1912	5.67	Ratio of emissivities, metal: black body
Gerlach }	1916	5.85	Mod ified Angstrom pyr heliometer
	1920	5.80	
Puccianti .	1912	5.96	Bolometer
Westphal .	1916	5.67	Ratio of emissivities, metal: black body
Keene .	1913	5.89	Thermometer
Coblentz .	1915	5.72	Modified Angstrom pyr heliometer
Kahanowicz	1917	5.61	Modified Angstrom pyr heliometer
Foote .	1918	5.70	Marvin pyr heliometer

Mean value of $\sigma = (5.72 \text{ to } 5.73) \times 10^{-5} \text{ erg. cm.}^{-2} \text{ sec.}^{-1} \text{ degree}^{-4}$

“It is shown from various experiments that, beyond all reasonable doubt, the total radiation emitted from a uniformly heated enclosure is proportional to the fourth power of the absolute temperature—the so-called Stefan-Boltzmann law. Furthermore, the tabulated data show that the numerical values of the majority of the various determinations of the coefficient σ , which enters into the mathematical formula of total radiation range about the value, $5.7 \times 10^{-5} \text{ erg. cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-4}$.”

The Constant c_2 of Spectral Radiation.

“Experimental evidence is cited showing that throughout the spectrum from 0.5μ to 50μ Planck's formula fits the observed spectral-energy distribution more closely than any other equation yet proposed. This formula is based upon theoretical principles, and after two decades of discussion it remains unchanged.”

PROBABLE VALUE OF THE CONSTANT c_2

Observer.	Date.	Observed.	Corrected.	c_2 Probable Value in Micron Degrees.
Paschen .	1899	2891	2891	14,360
Lummer and Pringsheim .	1900	2879	2879	
	—	2876	2876	
	—	2940	2882	14,300
Warburg .	1911 to 1915	—		14,300
Coblentz .	1913 to 1920	—		14,318

Average value of $c_2 = 14,320$ micron degrees.

"The numerical value of c_2 has fluctuated greatly in the various determinations. In the foregoing pages it is shown that this is owing to experimental difficulties, such as, for example, lack of precise knowledge of the temperature scale and of the refractive indices of the prisms used."

Confirmatory Evidence.

"One of the most interesting phases of the enquiry into the laws and constants of radiation is the confirmatory data which one obtains from a consideration of the interrelated phenomena of atomic structure, of X-rays, of ionisation and resonance potential, and of photo-electric action. From these data as well as from the foregoing data on the two constants of radiation one can compute the value of Planck's element of action, h . This gives seven independent methods of determining the universal constant, h . Or, from any one of four of these methods one can calculate the radiation constants (*cf.* Hennig, *Verh. Deutsch. Phys. Ges.*, **20**, 81 (1918); Birge, *Physical Rev.*, **14**, 361 (1919); Coblentz, *Bur. Standards Bull.*, **15**, 617 (1920) and it seems truly remarkable how close is the agreement with the observed values.

"For example, the writer's value of the coefficient of total radiation discussed on a preceding page is $\sigma = (5.72 \pm 0.012) \times 10^{-5}$ erg. cm.⁻² sec.⁻¹ deg.⁻²

This indicates a value of $c_2 = 14,320$ micron degrees and a value of $h = 6.55 \times 10^{-27}$ erg sec. The value of h determined by Blake and Duane by X-rays (*Physical Rev.*, **10**, 624 (1917)) is $h = 6.555 \times 10^{-27}$ erg sec., or an indicated value of $c_2 = 14,330$ micron degrees, which is close to experimental determinations of this constant.

"Again, starting with Warburg's value of $c_2 = 14,300$, the corresponding value of the coefficient of total radiation is $\sigma = 5.74 \times 10^{-5}$, which is the highest estimated limit of the average of twelve different determinations of this constant. Hennig (*loc. cit.*), on the basis of Sommerfeld's theory, the measurement of spectral lines, and the value of the electron, obtains $c_2 = 14,320$ and $\sigma = 5.717 \times 10^{-5}$."

“In summing up the evidence, it is of interest to include Birge's (*loc. cit.*) comprehensive and exact calculations of the constant h .”

BIRGE'S CALCULATION OF THE CONSTANT h .

Value of $h \times 10^{27}$		Remarks.
6.551 ± 0.009	$\sigma = 5.72 \times 10^{-8}$	Total radiation
6.557 ± 0.013	$c = 14,330$	Spectral radiation
6.542 ± 0.011	Rydberg constant	Bohr's theory of atomic structure
6.578 ± 0.026	Photo-electric equation	Einstein's equations
6.555 ± 0.009	X-rays	Quantum relation
6.560 ± 0.014	Ultimate Rational units	{ Theory of Lewis and Adams
6.579 ± 0.021	Ionisation potential	(<i>Physical Rev.</i> , 3, 92 (1914))

Mean value of $h = (6.5543 \pm 0.0025) \times 10^{-27}$.

“From this calculation and intercomparison by Birge of the data on c_2 , σ , and h , as determined by thermal radiometric, photo-electric, X-rays, and ionisation potential measurements, it appears that the value of h , computed from radiometric data, compares very favourably with that obtained by more direct measurement.”

“The outstanding disagreement between all the observed and computed data appears to be of the order of 1 to 3 parts in 1000, whatever the method of experimentation. This is a very close agreement, considering the variety of the data and the difficulties involved in making the experiments, which seems to indicate something more than a fortuitous relation between properties of matter.”

In conclusion it may be added that, to a close approximation, we have the following constants:—

$$A = \lambda_{\max}.T = 2885 \text{ micron degrees.}$$

$$c_2 = 14,320 \text{ micron degrees.}$$

$$\sigma = 5.72 \times 10^{-8} \text{ erg cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-4}.$$

$$h = 6.554 \times 10^{-27} \text{ erg sec.}$$

APPENDIX IV.

SOMMERFELD'S MODIFICATION OF BOHR'S THEORY OF THE ATOM.

By A. MCKEOWN.

Substitution of Elliptic Orbits for Circular Orbits.

(Sommerfeld, *Ann. Physik*, **51**, 1, 1916).

BOHR's initial treatment of the Rutherford atom model as expressed by equation 3 in Chap. V. is limited to electron movements in circular orbits about the nucleus, that is, the stationary system possesses one variable only, the angle swept out by the radius vector.

We owe to Sommerfeld and Wilson the generalisation of Bohr's principle of quantisation of angular momentum for periodic systems of several degrees of freedom, and by means of this Sommerfeld has shown how the primal assumption of elliptic orbits involving two independent variables leads to frequency relations identical with those of Bohr for circular orbits. Further, because of the modified interpretation of the results which is inherent in Sommerfeld's treatment, we are now able to take account of the fine structure exhibited by spectral lines, and to explain in more or less detail the observed effects of electric and magnetic fields on them.

Only a simple statement of the Sommerfeld treatment and its agreement with experimental observation will be given here.

For a system consisting of a massive nucleus (at rest) and a single electron revolving around it the position of the electron at any instant relative to the nucleus may, in the absence of external forces, be represented by two co-ordinates q_1 and q_2 ; for example, the polar co-ordinates ϕ and r . The kinetic energy T may be expressed as a function of q_1 and q_2 and their differential coefficients $\dot{q}_1$ and $\dot{q}_2$ with respect to time (*cf.* Appendix I., p. 310). The partial differential coefficients of T with respect to $\dot{q}_1$ and $\dot{q}_2$, written—

$$p_1 = \frac{\partial T}{\partial \dot{q}_1} \quad \text{and} \quad p_2 = \frac{\partial T}{\partial \dot{q}_2},$$

are termed the generalised momenta corresponding to the co-ordinates q_1, q_2 . In the case of circular motion of the electron round the nucleus, we may replace q_1 by ϕ , the angle which the radius vector makes at

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any instant with an arbitrarily fixed diameter, and q_1 by a , the radius of the circular orbit considered. The kinetic energy is given by—

$$T = \frac{1}{2}m_0a^2\left(\frac{d\phi}{dt}\right)^2 = \frac{1}{2}m_0a^2\dot{\phi}^2,$$

the angular velocity $\dot{\phi}$ being constant for circular motion. It follows that

$$p_1 = \frac{\partial T}{\partial \dot{\phi}} = m_0a^2\dot{\phi} = \text{angular momentum } M.$$

However, it will be remembered that Bohr's special assumption of orbital restriction can be written in the form—

$$M = \frac{nh}{2\pi},$$

where M is the angular momentum of the electron in its orbit, and n is a whole number. This is the condition which defines a particular series of orbits, out of the infinite number of dynamically possible orbits, as being stationary in the quantum sense.

It follows that Bohr's equation of restriction for circular orbits may alternately be written in the form—

$$\int p_1 dq_1 = \int M d\phi = 2\pi M = nh,$$

where the integration has been taken between the limits $q_1 = \phi = 0$ and $q_1 = \phi = 2\pi$, that is, for a complete revolution of the electron in its orbit.

It is easy to show that an equation of restriction of the same form $\int p dq = nh$ will, in the case of a linear oscillator, lead to the condition of elementary quanta of energy originally postulated by Planck. Consider a particle executing simple harmonic motion about a mean position. The only variable in this case is the distance x of the oscillator from its mean position, and the motion is defined by—

$$x = a \sin \omega t$$

where $\frac{\omega}{2\pi} = \nu$, the frequency of the oscillation. The kinetic energy at any instant is—

$$T = \frac{1}{2}m_0\dot{x}^2$$

so that p_x , the generalised momentum corresponding to the co-ordinate x , is given by—

$$p_x = \frac{\partial T}{\partial \dot{x}} = m_0\dot{x}.$$

Let us suppose that our equation of restriction is—

$$\int p_x dx = nh,$$

where the integration is taken over a complete period of the oscillation.

Changing from the variable x to the variable t and integrating, we have—

$$m_0 \int_{t=0}^{t=1/\nu} \dot{x} dx = \pi m_0 a^2 \omega = nh.$$

But the total energy of the vibrator is—

$$W = \frac{1}{2} m_0 a^2 \omega^2.$$

Hence :

$$W = nh \cdot \frac{\omega}{2\pi} = nh\nu.$$

which is identical with Planck's original assumption.

We now proceed to the case of motion in an elliptic orbit. Sommerfeld and other workers in this field have assumed that the general equations of restriction for the motion of an electron round a nuclear sun are of the form— $\oint p_s dq_s = n_s h$ where the integration is taken over

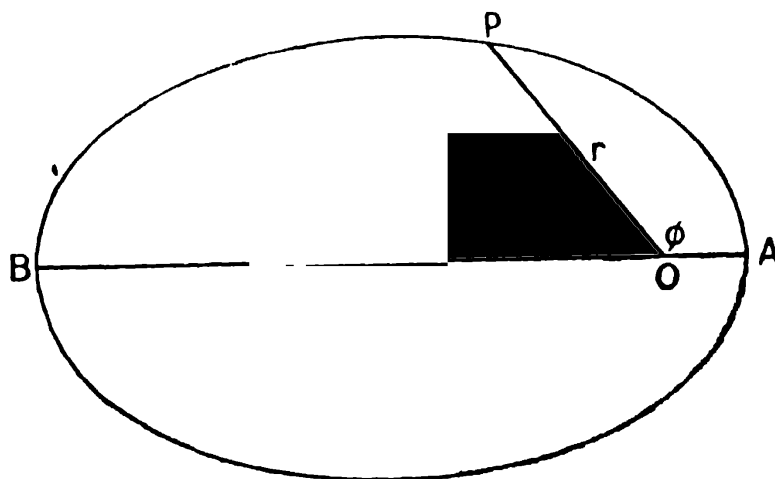


FIG. 21.

a complete libration of the q_s co-ordinate. There is one such equation of restriction for each co-ordinate, for each of which n_s is independently chosen. When the motion of the electron is strictly periodic, as for circular or elliptic orbits, there is no difficulty in fixing the limits of integration for each equation of restriction. Thus, for elliptic motion, the co-ordinates are $q_1 = \phi$ and $q_2 = r$ (see figure); q_1 is taken from $\phi = 0$ to $\phi = 2\pi$, and q_2 from $r = r_{\min.}$ (perihelion A) to $r = r_{\max.}$ (aphelion B) and back again, or what amounts to the same thing, from $\phi = 0$ to $\phi = 2\pi$.

Let us now consider an electron of mass m_0 and charge e at P moving in an elliptic orbit round a positive nucleus O at the focus of the ellipse. The charge on the nucleus is E , its mass is very great compared with m_0 so that the nucleus may be regarded as stationary. If the polar co-ordinates of P be (ϕ, r) , the velocity of the electron at any instant is $\frac{dr}{dt} = \dot{r}$ along OP, together with $r \frac{d\phi}{dt} = r\dot{\phi}$ perpendicular

to the line OP. The kinetic energy of the electron being $\frac{1}{2}m_0v^2$, where v is the resultant of these velocities, it follows that—

$$T = \frac{1}{2}m_0(\dot{r}^2 + r^2\dot{\phi}^2) \quad (1)$$

The potential energy V of the system is given by—

$$V = -\frac{eE}{r} \quad (2)$$

The generalised momenta corresponding to ϕ and r may be written as p_ϕ and p_r , and since these are defined by the relations—

$$p_\phi = \frac{\partial T}{\partial \dot{\phi}}; \quad p_r = \frac{\partial T}{\partial \dot{r}},$$

it follows that—

$$p_\phi = m_0 r^2 \dot{\phi}; \quad p_r = m_0 \dot{r} \quad (3)$$

The quantum equations of restriction are now—

$$\int_{\phi}^{\phi+2\pi} p_\phi d\phi = nh \quad (4)$$

and

$$2 \int_{r_{\min.}}^{r_{\max.}} p_r dr = \int_{\phi=0}^{\phi=2\pi} p_r dr = n'h \quad (5)$$

The coefficient 2 in the left-hand side of equation (5) allows for a complete libration of the electron in the elliptic orbit.

The factor $r^2 \dot{\phi}$ occurring in equation (3) is the area swept out by the radius vector r in unit time, and by Kepler's second law of planetary motion this area is a constant. Replacing p_ϕ by a constant p , the first equation of restriction (4) therefore reduces to—

$$2\pi p = nh \quad (6)$$

Again the equation of the ellipse in terms of its polar co-ordinates is—

$$\frac{1}{r} = \frac{1}{a} \frac{1 + \epsilon \cos \phi}{1 - \epsilon^2} \quad (7)$$

where ϵ is the eccentricity of the orbit and $2a$ is the major axis. By logarithmic differentiation of this equation with respect to ϕ we obtain—

$$\frac{1}{r} \cdot \frac{dr}{d\phi} = \frac{\epsilon \sin \phi}{1 + \epsilon \cos \phi} \quad (8)$$

But from equation (3) it follows that—

$$p_r = m_0 \dot{r} = m_0 \frac{dr}{d\phi} \cdot \dot{\phi} = \frac{p}{r^2} \cdot \frac{dr}{d\phi} \quad (9)$$

Also

$$dr = \frac{dr}{d\phi} \cdot d\phi.$$

Hence
$$p_r dr = p \left(\frac{1}{r} \frac{dr}{d\phi} \right)^2 d\phi = p \epsilon^2 \frac{\sin^2 \phi d\phi}{(1 + \epsilon \cos \phi)^2},$$

so that the second equation of restriction (5) reduces to—

$$p \epsilon^2 \int_0^{2\pi} \frac{\sin^2 \phi}{(1 + \epsilon \cos \phi)^2} d\phi = n' h,$$

or, using equation (6), to—

$$\epsilon^2 \int_0^{2\pi} \frac{\sin^2 \phi}{(1 + \epsilon \cos \phi)^2} d\phi = \frac{n'}{n} \quad (10)$$

Integration of equation (10) leads to—

$$\frac{1}{\sqrt{1 - \epsilon^2}} - 1 = \frac{n}{n'}$$

or

$$1 - \epsilon^2 = (n + n')^2 \quad (11)$$

The left-hand side of this equation depends only on the eccentricity ϵ , so that not only is the magnitude p , which determines the *size* of the orbit, quantised, but we see further that the eccentricity ϵ , which determines the *shape* of the ellipse, can only vary discontinuously, depending as it does on the ratio of two whole numbers n and $n + n'$.

Again, from equation (3) the kinetic energy of the electron is given by—

$$T = \frac{1}{2} m_0 (\dot{r}^2 + r^2 \dot{\phi}^2) = \frac{1}{2} m_0 \left(p_r^2 + \frac{p^2}{r^2} \right).$$

Whence, from equations (7) and (8)—

$$T = \frac{p^2}{m_0 a^2 (1 - \epsilon^2)^2} \left\{ \frac{1 + \epsilon^2}{2} + \epsilon \cos \phi \right\} \quad (12)$$

Also
$$V = - \frac{eE}{r} = - \frac{eE}{a} \frac{1 + \epsilon \cos \phi}{1 - \epsilon^2} \quad (13)$$

Since the sum of the kinetic and potential energies must be a constant, independent of the angle ϕ , the sum of the factors of $\epsilon \cos \phi$ in equations (12) and (13) must be equal to zero. This leads to—

$$\frac{p^2}{m_0 a^2} \frac{1}{(1 - \epsilon^2)^2} = \frac{eE}{a(1 - \epsilon^2)}$$

or

$$p^2 = m_0 e E (1 - \epsilon^2) \quad (14)$$

Applying equations (6) and (11), we obtain—

$$a = \frac{h^2}{4\pi^2 m_0 e E} (n + n')^2; \quad b = \frac{h^2}{4\pi^2 m_0 e E} n(n + n') \quad (15)$$

where $2b$ is the minor axis of the ellipse.

If W be the work required to remove the electron from its orbit to an infinite distance away, it is clear that—

$$-W = T + V = \frac{eE}{a(1 - \epsilon^2)} \left\{ \frac{1 + \epsilon^2}{2} - 1 \right\} = -\frac{eE}{2a} \quad (16)$$

Substituting the value of a given by equation (15), it follows that—

$$W_{n, n'} = \frac{2\pi^2 m_0 e^2 E^2}{h^2} \cdot \frac{1}{(n + n')^2} \quad (17)$$

the suffices n, n' being introduced to denote the state of the orbit.

If we now assume with Bohr that a change of the system from the state characterised by the quantum numbers m, m' to that characterised by n, n' is accompanied by emission of a quantum of homogeneous radiation of frequency ν , we have—

$$\nu = \frac{2\pi^2 m_0 e^2 E^2}{h^3} \left\{ \frac{1}{(n + n')^2} - \frac{1}{(m + m')^2} \right\} \quad (18)$$

Since n, n', m, m' are any integers, it is evident, on comparison with the simpler Bohr treatment given by equations (3) and (4) in Chap. V., that the foregoing analysis of elliptic orbits leads to exactly the same spectral series as is predicted on the basis of circular orbits.

However, the physical significance of the two results is very different.

Thus if we write the series predicted by the earlier Bohr theory in the form—

$$\frac{2\pi^2 m_0 e^2 E^2}{h^3} \left\{ \frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right\},$$

the Balmer series in the hydrogen line spectrum is obtained by placing $\tau_2 = \infty$; $\tau_1 = 3, 4, 5 \dots$; whilst the more complete formulation, as contained in equation (18), predicts the Balmer series for *any* set of integral values of n, n', m, m' which makes $n + n' = 2, m + m' = 3, 4, 5 \dots$. It should be noted that all the elliptic orbits which possess the same value of $n + n'$ or W have the same value of $2a$, so that in the production of a single line all the initial orbits which will give rise to the emission have the same major axis, and similarly for all the final orbits. The values $n' = 0, m' = 0$ correspond to zero eccentricity, that is circular orbits, so that for these values the system reduces to the simple Bohr configuration. The values $n = 0$ and $m = 0$ must be excluded since either would represent a rectilinear orbit passing through the nucleus. Omitting these, it is evident that the first line of the Balmer series, which corresponds to $n + n' = 2, m + m' = 3$ can be generated in six different ways, and should therefore represent the superposition of six spectral lines. The second line of the series, given by $n + n' = 2, m + m' = 4$ can be arrived at in eight different ways, the third line of the series in ten ways, and so on.

Whether or not all these *apparently* possible modes of generation of a single spectral line are dynamically possible need not seriously concern us unless we have at our disposal some means of resolving the apparently homogeneous line into its constituents. As previously mentioned, such means are available and will be discussed in the following sections. Two general laws, embodied respectively in Rubinovicz's Principal of Selection and Bohr's Principal of Correspondence have been utilised in investigating the dynamical probability of the occurrence of any particular transit between stationary states, and although semi-empirical in nature, both Principles—and especially that of Bohr—have met with considerable success in this connection. It is not proposed, however, to discuss these theories in detail here (*cf.* Appendix V.). [An excellent account of their theoretical basis and applications to particular cases will be found in Sommerfeld's *Atombau und Spektrallinien* (3rd Ed. *English trans.*, Methuen, 1923).]

The Fine Structure of Emission Lines.

To test the truth of Sommerfeld's modification of Bohr's treatment, it is essential that the apparently homogeneous line—

$$\nu = \frac{2\pi^2 m_0 e^2 E^2}{h^4} \left\{ \frac{1}{(n + n')^2} - \frac{1}{(m + m')^2} \right\},$$

should be resolved into its constituents and these separate lines rendered amenable to direct spectroscopic observation. For this purpose we require the action of a field whose effect on the energy content of the atomic system considered above will vary with the shape or eccentricity of the electron's orbit round the nucleus. Such an influence is found in the atom itself in the relativistic factor which has been hitherto neglected in our dynamical treatment of the system. Bohr has emphasised the importance of the introduction of the effect of the velocity of the electron on its mass (and therefore its orbit), and has proposed to view the doublets observed in the hydrogen spectrum as a relativistic phenomenon. Sommerfeld, however, attacks the problem, not by modifying the Bohr circular orbits in this sense but by applying the necessary corrections directly to his more general treatment of the preceding section. The mass of the electron is not accurately a constant, but depends on the velocity with which it travels according to the equation

$$= m_0 / \sqrt{1 - \frac{v^2}{c^2}},$$

where v is the velocity relative to the observer and m_0 is the mass at rest relative to the observer. When this modification is taken into account, the motion of the electron round the nucleus is no longer an ellipse nor is it strictly periodic, but for moderate velocities of the electron, its motion may be represented by an ellipse which undergoes a slow progression of the apses. This type of motion is termed conditionally

periodic, in that the limits of the variables ϕ and r are quite definite and fixed, but for successive revolutions r does not attain its limits for the same values of ϕ .

The final result of the relativistic correction is to replace equation (17) by

$$W_{nn'} = \frac{2\pi^2 m_0 e^2 E^2}{(n + n')^2 \hbar^2} \left\{ 1 + \left(\frac{2\pi e E}{\hbar c (n + n')} \right)^2 \left(\frac{1}{4} + \frac{n'}{n} \right) + \dots \right\} \quad (19)$$

where c is the velocity of light and the other symbols retain their previous significance. This is an expansion in terms of $\left(\frac{2\pi e E}{\hbar c} \right)^2$, and since this quantity is of the order 5×10^{-5} , it is evident that for practical purposes all terms beyond the second may be neglected.

Hence the relativity correction consists of two parts—

I. An increase in $W_{n, n'}$ by a factor

$$+ \frac{1}{4} \left\{ \frac{2\pi e E}{\hbar c (n + n')} \right\}^2 = 1 + \frac{W_{n, n'}}{2m_0 c^2},$$

II. A further increase in $W_{n, n'}$ by an amount equal to $\frac{4n'}{n}$ times the first correction.

For circular orbits $n' = 0$, and the second correction disappears. Since the first correction does not depend on n and n' separately, it will not cause the splitting of a line into its components, so that for circular orbits we should obtain no fine structure. It will, however, cause a slight displacement of the line as a whole from the position calculated on the basis of no relativistic effect, and is therefore called by Sommerfeld the "relativistic correction for circular orbits". The fine structure of lines depends on the second correction, which, since it contains the integers n and n' separately, will have slightly different values for different eccentricities of the orbits characterised by the condition $n + n' = a$ constant. Hence for two orbits $W_{n, n'}$ and $W_{m, m'}$, if both $W_{n, n'}$ and $W_{m, m'}$ can have a number of distinct but only slightly different values found by putting $n + n' = a$ constant, $m + m' = a$ constant, the value of ν resulting from the equation

$$h\nu = W_{n, n'} - W_{m, m'} \quad (20)$$

will similarly possess a number of distinct and slightly differing values. In this way Sommerfeld accounts for the multiplicity of lines in the emission spectra of hydrogen and helium.

It should first be noted, however, as a consequence of formulæ (19) and (20), that the Rydberg constant in the Balmer series of hydrogen, instead of being equal to $\frac{2\pi^2 m_0 e^4}{\hbar^3}$, the value predicted by the Bohr treatment of circular orbits, should vary slightly from line to line according to the equation—

$$N = N_0 \left\{ 1 + \frac{\pi^2 e^4}{\hbar^2 c^2} \left(\frac{1}{4} + \frac{1}{m_1} \right) \right\}$$

where m_1 has the values 3, 4, 5, etc. If ΔN denote the difference between the constants for two different lines, the observed and predicted values of the expression $10^6 \cdot \frac{\Delta N}{N_n}$ are quoted by Sommerfeld as—

	$H_\alpha - H_\beta$	$H_\alpha - H_\gamma$	
Observed	0.37	0.35	0.06
Predicted	0.61	0.89	1.04

The agreement is satisfactory as regards sign and order of magnitude.

Let us now examine more closely the fine structure to be expected in the lines of the Balmer series. The final state of the atom in the generation of any line of this series corresponds to $n + n' = 2$, so that *two* final orbits are possible in the generation of each line, a circular orbit given by $n = 2$, $n' = 0$, and an elliptic orbit given by $n = 1$, $n' = 1$ (as mentioned above, the arithmetic combination $n = 0$, $n' = 2$ is to be excluded on physical grounds). If we therefore omit for the moment the varying multiplicity of the initial orbits, it follows from equations (19) and (20) that each "line" of the series should at least consist of a doublet, the wave-number difference for each doublet having the same numerical value which is readily calculated to be 0.365 cm.^{-1} . Actually, such a structure is observed in the hydrogen emission spectrum. Each "line" of the series is found to contain this doublet, and the wave-number difference of the components, whilst varying slightly from member to member of the series, has a mean value approximating closely to 0.365 cm.^{-1} . If now we take into consideration the multiplicity of initial orbits in the generation of a Balmer "line," we should expect the number of observed components of any one line to be much greater than two. Thus for H_α which corresponds to $n + n' = 2$, $m + m' = 3$, the total possible transitions are six in number. However, only three of these predicted lines are observed, namely those corresponding to the changes $2, 1 \rightarrow 1, 1$; $3, 0 \rightarrow 2, 0$; and $1, 2 \rightarrow 2, 0$. The latter pair of lines form the H_α doublet already referred to. The absence of the other three constituents is fully accounted for by the Principles of Selection and Correspondence previously mentioned. In this particular case, only those transitions are dynamically possible for which the difference in the azimuthal partial quantum numbers n and m is ± 1 . Similarly in the case of H_β , for which $n + n' = 2$, $m + m' = 4$, five out of the eight seemingly possible components are disallowed.

Observations with hydrogen are especially difficult because of the very small separation of the lines to be expected, and the relatively great broadening of individual lines due to the Doppler effect. If, instead, the spectrum due to ionised helium be investigated, the mathematical analysis developed for hydrogen still holds good, but the

Doppler effect is considerably decreased for the same temperature of the gas, and the separations predicted are all multiplied sixteen-fold on account of the factor β^4 in the second relativistic correction. In this particularly favourable case, the results of Sommerfeld's analysis are completely vindicated. The helium series consists primarily of well defined doublets, the value of whose wave-number difference is found by Paschen to be $16 \times 0.3645 \text{ cm.}^{-1}$, in agreement with the calculated figure for hydrogen given above. Further, the number and intensities of the subordinate components due to multiplicity of initial orbits are in complete harmony with the predictions of the Correspondence and Selection Principles. The details of this example are given very fully by Sommerfeld, *loc. cit.*

Recently, certain very careful measurements have been carried out by McLennan and Shrum (*cf. Nature*, August 4, 1923) on the doublet separations for the principal lines of the Balmer series of hydrogen. The results obtained are tabulated below :—

Line	Wave-length.	Separation of Components (Wave-number Differences).	Probable Error.
H _{α}	6562.79	0.33 cm. ⁻¹	0.02 cm. ⁻¹
H _{β}	4861.33	0.36 "	0.01 "
H _{γ}	4340.46 Å	0.37 "	0.02 "
H _{δ}	4101.73 Å	0.36 "	0.02 "
H _{ϵ}	3970.07 Å	0.35 "	0.02 "

These data afford a striking confirmation of the Sommerfeld theory of the fine structure of emission lines.

Stark Effect for Hydrogen.

(Epstein, *Ann. Physik*, 50, 489, 1916.)

It has been found experimentally by Stark that the presence of a strong electric field causes an apparently homogeneous¹ spectral line of the Balmer series to break up into a number of lines whose frequencies form simple arithmetic series on either side of the frequency of the undisturbed line. The extent of the separation of these resultants is proportional to the strength of the imposed field. The total number of resultants obtained from any single Balmer line does not depend on the field but increases with the frequency or series number of the original line considered. When observed in a direction perpendicular to the lines of force of the electric field, all the components are found to be plane-polarised, some parallel to the field, some perpendicular to it. When viewed along the direction of the field, the former components do not appear, but the latter are visible and are unpolarised.

¹ In this section we speak of the observed lines H _{α} , H _{β} , etc., of the undisturbed spectrum as homogeneous, since the separation to be considered here is of a much greater order than that of the fine structure discussed above.

Epstein has investigated this effect from the theoretical standpoint, using the same fundamental principles as were laid down by Sommerfeld in his treatment of the undisturbed motion of the atomic system. The analysis is necessarily rendered more complex by the appearance of a third degree of freedom to take account of the orientation of the system relative to the electric field. This involves quantising separately with respect to each of the three variables concerned. Epstein's final result for the total energy of the system under the influence of the field may be written—

$$W_{n, n', n''} = \frac{2\pi^2 m_0 e^2 E^2}{h^2} \left(\frac{1}{(n + n' + n'')^2} + \frac{3h^2 X}{8\pi^2 m_0 e E} (n + n' + n'')(n - n') \right) \quad (21)$$

where X is the intensity of the applied field, n, n', n'' are integers defining the stationary state of the system, and the other symbols retain their previous significance. This equation corresponds to equation (17) of the first section. It should be noted here that the value $n'' = 0$ is excluded (as was $n = 0$ in the case of the undisturbed motion) since this value would signify an electron orbit passing sooner or later through the nucleus.

If $n + n' + n''$ be replaced by n_1 , and $m + m' + m''$ by m_1 , the frequency of the light emitted when the electron passes from the state m, m', m'' to the state n, n', n'' is given by—

$$\nu = \frac{2\pi^2 m_0 e^2 E^2}{h^3} \left(\frac{1}{n_1^2} - \frac{1}{m_1^2} \right) + \frac{3hX}{8\pi^2 m_0 e E} \left\{ n_1(n - n') - m_1(m - m') \right\} \quad (22)$$

The first term on the right hand side is the well-known Bohr expression for the undisturbed spectral line, the second term represents the extent of the splitting produced by the electric field X . It is evident that this will differ for each component of the original "homogeneous" line, since each component depends on a characteristic combination of the integers n, n', n'' and m, m', m'' . Now $n_1(n - n') - m_1(m - m')$ is necessarily an integer, so that the displacement produced by an electric field X may be written—

$$d\nu = \frac{3hX}{8\pi^2 m_0 e E} \cdot P = A \cdot P \cdot X \quad (23)$$

where P is a variable whole number and A is a constant, completely defined by the constants of the atomic system. It follows that under the influence of a given electric intensity X , the components of any line should be spread out to form a regular series of equidistant lines, the distance between consecutive lines having a constant value AX . Also, since n, n' enter symmetrically into the deduction of equation (21), any negative value of $(n - n')$ should be equally as likely as the same positive value of $(n - n')$, so that the components should be arranged symmetrically about the position of the original line. Again, other things being equal, it is obvious that the greater the value of m_1 the greater will be the number of different values which the factor

P can assume, that is, the number of components obtained from a single Balmer line should increase with its series number. All these results are in complete agreement with the experimental evidence of Stark.

The Principles of Selection and Polarisation of Rubinoviez have been used to fix the number of units by which the equatorial partial quantum number m'' may change, and the state of polarisation of the resulting lines. The only possible changes in the equatorial quantum number are found to be 0 and ± 1 . In the first case, $m'' = n''$, and any line which involves the constancy of this partial quantum number in its production will be plane-polarised parallel to the lines of force of the field. In the second case, $m'' = n'' \pm 1$, and the emitted radiation will be circularly polarised around the direction of the lines of force. These rules are sufficient to account for the observed states of polarisation of all the different components arising out of the Balmer series. Some of the lines predicted by the Principle as possible are not observed, but this might be accounted for by considerations of the very feeble intensity of these radiations. Indeed, Kramers has shown, on the basis of the more complete Principle of Correspondence, that the intensities of the lines in question are vanishingly small, and therefore should not be observed.

The case of the line H_β in the hydrogen spectrum might be quoted as an instance of the general agreement between Epstein's predictions and actual observation. The possible values of P in equation (23) are here considered to be 14, 12, 10, . . . 2, 0. All the corresponding lines with the exception of $P = 14$ are observed. The following table gives the calculated and observed values of $\Delta\lambda$, the extent of the displacement in Angstrom units.

		P = 12	10	8	6	4	2	0
$\Delta\lambda$	Calcd.	19.4	16.1	12.8	9.7	6.5	3.2	0
	Obsd. (a)	19.4	16.3	13.2	10.0	6.7	3.3	0
	Obsd. (b)	19.3	16.4	13.2	9.7	6.6	3.4	0

The third and fourth rows refer to light polarised so that the electric force is parallel and perpendicular respectively to the lines of the external field. The general agreement between the observed and the calculated values is very good. Further figures for H_α , H_γ and H_δ will be found in Epstein's original paper.

The Normal Zeeman Effect.

(Sommerfeld, *Physik. Zeitsch.*, **17**, 491, 1916).

This effect may be quoted as another illustration of the general applicability of Sommerfeld's method of quantisation of the variables of a system of more than one degree of freedom.

When a powerful magnetic field acts on any line of the simpler spectral series (originating from atomic systems of the hydrogen type), it is found to cause a resolution of the line into either doublets or

triplets, according to the direction of observation of the phenomenon relative to that of the imposed field. When examined along the magnetic lines of force, two spectral lines are seen displaced to equal extents on either side of the position of the original line, which, however, does not appear. These two lines are found to be circularly polarised in opposite senses. Viewed perpendicular to the direction of the field, three lines are seen; one, which is plane-polarised with the electric vector parallel to the field, coincides in position with the undisturbed line; the other two occupy the same positions in the spectrum as the components of the doublet just referred to, but are now seen to be plane-polarised with the electric vectors perpendicular to the direction of the field.

On the basis of the classical electron theory, Lorentz has been able to deduce theoretically all the details of this, the normal Zeeman Effect. Besides predicting correctly the type of resolution to be expected and the sense of the polarisation of each component, Lorentz obtains an expression for the displacement of the components relative to the position of the undisturbed line, *viz.* $d\nu = \frac{eH}{4\pi mc_0}$, which is in complete

accord with observation. In this equation, H denotes the intensity of the magnetic field and the other symbols retain their usual significance. When we consider that classical theory affords no explanation of the production of the simplest spectral lines or of the observed effects of electric fields on the same, it is remarkable that such a complete and ready explanation of the Zeeman Effect is forthcoming. The nature of the radiation process which is assumed by Lorentz bears no apparent resemblance whatsoever to that which is fundamental to Bohr's theory of the origin of spectra. Whilst no explanation of the apparent anomaly is suggested, it is obviously of special importance to investigate the theory of the Zeeman Effect along analogous lines to those which have already proved successful in the interpretation of spectra, both undisturbed and under the influence of electric fields. This has been done by Debye and by Sommerfeld. Their analysis of the problem, taken in conjunction with either the rules of Selection and Polarisation of Rubinovicz or the Principle of Correspondence of Bohr, leads to exactly the same results as does the older theory of Lorentz.

Three independent variables are obviously necessary in order to represent the motion of a simple nucleus-electron system of the hydrogen type in a magnetic field. The variables used by Sommerfeld are the familiar polar space co-ordinates (r, θ, ϕ), the direction of the axis of r coinciding with the direction of the applied field. The motion is quantised separately with respect to each of these variables according to the conditions:—

$$\begin{aligned} \int p_r dr &= n_1 h, \\ \int p_\theta d\theta &= n_2 h, \\ \int p_\phi d\phi &= n_3 h. \end{aligned}$$

The result of the operations is that the total energy of the system in the presence of a magnetic field of strength H is given by the relation:—

$$-W = -W_0 + n_3 \cdot \frac{h e H}{4 \pi m_0 c},$$

where $-W_0$ is the total energy of the system in the absence of the field. It should be noted that only the equatorial quantum number n_3 occurs in the correcting factor introduced as a result of the field.

We may now apply this expression for the energy in Bohr's frequency relation to obtain the frequency of the spectral line generated by the transition:—

$$(m_1 m_2 m_3) \rightarrow (n_1 n_2 n_3).$$

This gives—

$$\nu = \nu_0 + (m_3 - n_3) \cdot \frac{e H}{4 \pi m_0 c}.$$

Here ν_0 denotes the difference in the values of the total energy in the absence of the field divided by h , and ν_0 is therefore the frequency of the undisturbed line. Thus, in the normal Zeeman Effect, we should expect a series of equally spaced lines on either side of the central line ν_0 corresponding to the different values, positive and negative, which $(m_3 - n_3)$ may assume.

As in the case of the Stark Effect, however, the Principle of Selection limits the change in the equatorial quantum number m_3 to ± 1 and 0. In the first case, the frequencies of the resulting spectral lines are given by:—

$$\nu = \nu_0 \pm \frac{e H}{4 \pi m_0 c}.$$

Again, according to the rule of Polarisation previously stated, each of these lines is circularly polarised in a plane perpendicular to the field, and should therefore appear circularly polarised when viewed longitudinally and plane-polarised perpendicular to the lines of the field when viewed transversely. For a transition involving no change in the value of m_3 , the resulting line should be coincident with the position of the line in the absence of the field, and should be plane-polarised with its electric vector parallel to the direction of the field. This line, therefore, should only appear when viewed transversely. Obviously, all these results of the quantum analysis are in agreement with the observed details of the normal Zeeman Effect already given.

It is, perhaps, significant that in the final expression for the normal Zeeman separation the constant h , which is essentially of quantum origin, does not explicitly appear. This is in contra-distinction to the occurrence of h in the corresponding frequency displacements of the Stark Effect and in the general quantum formulation of series relations. As previously pointed out, however, the Zeeman Effect alone lends itself to quantitative treatment along the lines of classical theory. The complete agreement of the final results of the classical and quantum methods in the realm of magneto-optics supports to some extent the basic idea of an intimate connection between the classical and quantum

views of radiation phenomena on which Bohr's Principle of Correspondence is founded.

Only the normal Zeeman Effect, as given experimentally by the lines of hydrogen and helium, has been touched upon in this section. In general, however, the action of a magnetic field on spectral lines is of a more complicated nature. With either of the sodium D lines, for example, many more components than the three predicted by the above theory are observed, and the spacing of the components, whilst following relatively simple laws, does not correspond to the theoretical spacing

$$d\nu = \frac{eH}{4\pi m_0 c}$$
 This—the anomalous Zeeman Effect—is naturally a

consequence of the departure of the emitting atomic system from the simple model employed in the fore-going analysis. Using the methods of classical electron theory, Voigt (*Ann. Physik*, **41**, 403; **42**, 210, 1913) has derived equations which serve to explain the entire behaviour of the sodium D lines under the influence of magnetic fields. Voigt's theory of the anomalous Zeeman Effect thus corresponds to the Lorentz theory for the normal effect already mentioned. Recently Sommerfeld (*Zeitsch. für Physik*, **8**, 257, 1922) has modified the treatment of Voigt in terms of quantum dynamics, and has succeeded in systematising all the known modifications of the anomalous effect in the form of certain relatively simple equations. Certain arbitrary assumptions made by Sommerfeld have been given a definite physical interpretation by Heisenberg (*Zeitsch. für Physik*, **8**, 273, 1922) in terms of the atomic structures of the systems concerned.

APPENDIX V.

THE CORRESPONDENCE PRINCIPLE.

BY JAMES RICE, M.A.

IT is a commonplace to compare an atom to an astronomical planetary system, but the analogy is far from perfect. Considering it from the standpoint of pure dynamics we recognise that the advent of a disturbing body will alter the orbits in a planetary system and that there will be no return to the original orbits on the departure of the intruder. On the other hand, although we are bound to admit that any disturbing influence may alter the electronic orbits of an atomic system, the alteration will disappear on the removal of the influence. It is impossible to account for the permanent properties of the elements otherwise. There appears to be for any atomic type a normal state (which must mean in modern atomic theory, a normal group of orbits) which persists and is independent of all so-called "initial conditions," a state of affairs of which there is no analogue in a planetary system. The point of contact between atomic theory and classical dynamical theory consists in the fact that the special group of orbits are assumed to obey the classical laws of motion, the electrons being subject to an inverse square attraction to the nucleus, *i.e.* the orbits are "mechanically possible," but pure dynamics affords no reason whatever why this special group of orbits should be favoured at the expense of the infinity of orbits which are just as "mechanically possible."

When we consider the orbits of electrons in atoms from the point of view of electrodynamics we realise a still further difficulty for classical theory, for, under these circumstances the electrons should be radiating energy continuously and in consequence their orbits should be slowly contracting. Thus even apart from encounters with neighbouring systems the permanence of the normal orbits required by the permanence of the properties of any given element would not be ensured.

In face of the breakdown of accepted principle there is nothing for it but to frame new hypotheses to meet the situation, and in accordance with all the canons of good reasoning these new hypotheses must be as few as possible and make as little breach as possible with the previous standpoint. The hypothesis put forward by Bohr during the past decade are at present accepted as conforming to that criterion.

In the first place, Bohr assumes that there are in addition to the normal orbits referred to above other "mechanically possible," orbits of

greater energy which are specially favoured. An electron can remain circulating for a finite time in one of these without radiating. As before no criterion can be found in the older dynamical and electrodynamical theory for selecting such orbits or endowing them when so selected with the non-radiating property. A method of selection has been highly developed in the more simple types of systems and appears to be equally valid in more complex atoms, although the application is correspondingly difficult. It is a purely dynamical problem and its solution in general employs a mathematical technique due to Hamilton and Jacobi and well known to astronomers dealing with planetary perturbations in astronomical theory. The method calculates for any mechanically possible orbit a series of quantities called "moduli of periodicity."¹

The value of any modulus may, as far as pure dynamics is concerned, have any one of an infinity of values. The method of selection suggested by Bohr, Sommerfeld and their co-workers has been to choose those orbits in which each of the moduli is some *integral* multiple of the Planck constant h . In general this criterion gives sufficient equations to define the orbits uniquely. These "quantum favoured" or "quantised" orbits are then assumed to be "non-radiating," *i.e.* that an electron circulating in one of these will not radiate in the classical continuous manner so that it will persist in the orbit for a finite time. (This method is explained more fully in the case of the simpler atoms in Appendix IV^a.) However, the electron does not remain perpetually even in a quantised orbit. Under the influence of external radiation, of the approach of another electron or of some, as yet ill-defined, inherent property (bearing a resemblance to the spontaneous activity responsible for radioactive phenomena), an electron may leave a quantised orbit. It does not do it as far as we can judge by the slow contraction process considered in electrodynamic theory. At present no assumption as to the method of departure has been put forward with any serious claims to consideration, nor as to what takes place until the electron once more takes up a temporary "mechanical" life in another quantised

¹ In the general treatment of a dynamical system, there enters a dynamical concept of the highest importance, known as *action* (which is not to be confused with the use of that word in the third of Newton's well-known laws of motion).

If we multiply twice the kinetic energy of the system at an instant by the magnitude of a succeeding element of time, the product is known as the accumulation of action during that element of time. If we integrate this result over a finite lapse of time we obtain the action accumulated by the system during that interval. The amount accumulated in the time reckoned from a defined original instant is usually referred to as the *action* of the system.

Now although the following statement has not been proved to possess universal validity, yet in all the cases of atomic systems so far investigated it has been found possible to choose the co-ordinates of the system in such a way that the action can be equated to the sum of a number of parts, the number being the same as the number of co-ordinates required to define the system completely, and each part depending entirely on the initial and final values of one co-ordinate (together with certain constants which help to define the configuration and motion of the system at the original instant). The amount by which any one of these partial actions increases during one period of the corresponding co-ordinate is called a *modulus of periodicity*. There are obviously as many moduli as there are co-ordinates.

orbit. The old and new orbits differ in energy, and so the atom is supposed to emit a mono-chromatic radiation if the former has greater energy than the latter. In the contrary case absorption takes place. In both cases the frequency is given by the quotient of the energy-difference by h . The normal state of the atom would be that configuration of the electrons among all the possible quantum-favoured configurations which corresponds to the minimum energy.

On reviewing the situation at this point we see that although a certain part of the classical theories has been discarded as inadequate, another part is retained. Thus the quantised orbits are mechanically possible. Now it is a further noteworthy fact that in the domain of full temperature radiation the conclusions of quantum theory and classical theory are in good agreement for conditions of high temperature or low frequency—there is a certain “correspondence” between the two views in a limited region. Another correspondence was pointed out by Bohr in his earliest papers on atomic theory, and the recognition of it led to one of the first triumphs of his theory, *viz.* the expression of a formal relation between the Rydberg spectral constant and the constants h , e and m . Thus taking the simplest of atoms, the hydrogen, experiment shows that the formula for the spectral lines of the Balmer’s series is—

$$= K \left(\frac{1}{\tau'^2} - \frac{1}{\tau''^2} \right),$$

where K is the Rydberg constant and τ' and τ'' are two integers ($\tau' > \tau''$). This would imply on the Bohr theory that the energy for a quantised orbit of the electron (ellipse or circle) would be given by—

$$E_\tau = C - \frac{K/h}{\tau^2}, \quad (1)$$

where C is a constant, *viz.* the energy when the electron is at rest at an infinite distance from the nucleus. Each orbit would be to some extent characterised by its (total) quantum number τ , the 1-orbits having the least energy, the 2-orbits, 3-orbits, etc., having successively increasing energies.

Now ordinary dynamics proves, for an elliptical orbit, described by a mass m round a centre of force attracting it according to the law μ/r^2 , where μ is a constant, that—

$$\omega = \sqrt{\frac{2W^3}{\pi^2 \mu^2 m}}, \quad a = \frac{\mu}{2W} \quad (2)$$

where ω is the number of revolutions per second round the focus, a the semi-major axis of the ellipse and W the work required to remove m to infinity from the orbit.

In the case of the hydrogen atom m is the mass of an electron, μ is the square of the electronic charge e , and by (1)

$$W = \frac{K/h}{\tau^2}$$

for a τ -orbit; so that for this orbit equations (2) become

$$\omega = \left(\frac{2K^3 h^3}{\pi^2 \tau^6 e^4 m} \right)^{1/2}; \quad a = \frac{2e^2 \tau^2}{K h} \quad (3)$$

Reverting to the idea of a possible correspondence we see that the frequencies of the emitted radiation are given by (1); *that is, experimental fact.* According to classical electromagnetic theory, the frequencies of emitted radiation should be given by the first of equations (2); for in that theory the frequencies agree with the frequency of vibration or revolution of an electron and integral multiples of it. Now from what we know about theory and experiment in the case of the hohlraum, we might expect a correspondence or agreement between the two views in the case of comparatively low frequencies, *i.e.* for orbits with large quantum numbers. Thus from (1)

$$\begin{aligned} \nu &= K \left(\frac{1}{\tau'^2} - \frac{1}{\tau''^2} \right) \\ &= K(\tau' - \tau'') \cdot \frac{\tau' + \tau''}{\tau'^2 \tau''^2} \end{aligned}$$

Suppose τ'' is a large number, and τ' a number slightly greater so that, $\tau' = \tau + k$ where k is an integer small compared to τ . Then approximately

$$= k \frac{2K}{\tau^3} \quad (4)$$

Thus according to (4) in this region (*i.e.* infra-red) the radiation would consist of lines whose frequencies are approximately a harmonic series built on a fundamental frequency $2K/\tau^3$ and would be due to electrons jumping to the τ orbit from orbits adjacent to it but possessed of larger energy. But by classical theory revolution of an electron in the τ -orbit would also give a harmonic series of lines whose fundamental frequency would be the ω given by (3). If there is to be agreement between the two views in this region

$$\frac{4K^2}{\tau^6} = \frac{2K^3 h^3}{\pi^2 \tau^6 e^4 m}$$

The particular number of the orbit cancels out and we have the following formula for the Rydberg constant—

$$K = \frac{2\pi^2 m e^4}{h^3}$$

which is in excellent agreement with experimental values of K , e , m , h .

These considerations show that the classical theory is not to be cast aside entirely as useless. In our present position it may be of assistance where our as yet imperfectly developed body of quantum principles fails to give us a clear lead. This statement receives an ample justification

in the fact recently discovered by Bohr that on questions concerning not the frequency alone of emitted or absorbed light, but also its state of polarisation and its intensity (matters on which simple quantum theory affords us no direct guidance) the classical theory comes to our aid and supplies us with the necessary data for an approximate solution of the rather difficult statistical problems involved. In elucidating this further point of contact between the old and new, Bohr was led to a view which he calls the *Principle of Correspondence*. We may, before proceeding to define it more clearly, state it broadly in the following way:—

A study of any atomic system leads to the recognition of sets of quantised orbits among the infinity of mechanically possible orbits of each electron. The motion of an electron in an orbit can be regarded as the resultant of three linear vibrations, each component being parallel to one of the co-ordinate axes. Further, each of these vibrations can be regarded as the sum of a number of different, but simultaneously existing, "simple harmonic vibrations" whose frequencies bear simple numerical relations to one another.

The method of analysing a compound oscillation into its simple harmonic constituents was first discovered by Fourier, and so this analysis is referred to as "Fourier analysis" and the separate constituents as forming a "Fourier series".

We shall call the frequency of any of the simple harmonic constituents into which the complex actual motion can be analysed, a harmonic "mechanical" frequency. Classical electromagnetic theory deduced the results that the emitted light should consist of lines having "optical" frequencies equal to the harmonic "mechanical" frequencies and also that the intensity and polarisation of the emitted mono-chromatic radiations should be determined by the nature of certain coefficients in the "Fourier series" of the motion of the electron. Quantum theory, on the other hand, discards the classical deduction concerning the agreement of the optical frequencies and mechanical frequencies. In its place it sets up a new method of calculating the optical frequencies by means of the series of all possible leaps between the members of the group of quantised orbits. But in the lately enunciated *Principle of Correspondence* Bohr proposes to make use of the other deductions of classical theory concerning intensity and polarisation of the light. Thus we have a series of simple harmonic terms in the Fourier analysis of the electron motion; we also have a series of possible quantum jumps. It is possible to set up a correspondence between the Fourier terms and the quantum jumps, so that to any quantum jump between two definite orbits there corresponds one, and only one, term of the Fourier series. (The method of setting up the correspondence will be outlined presently.) The principle postulates that the information supplied by classical theory concerning the polarisation and intensity of the mono-chromatic light, which according to the older idea should be present in the emitted light and have an optical frequency equal to the mechanical frequency of a given Fourier constituent, is approximately true for the line actually present in the emitted light whose optical frequency is given by the quantum leap corresponding to the Fourier term in question; further, the approximation

is nearer to the truth as the quantum numbers of the orbits in question increase and the frequencies decrease.

In order to apprehend the principle more clearly than is possible through the previous paragraph, it will be necessary to acquire some familiarity with the harmonic analysis of expressions representing oscillating quantities. The basis of this is the famous theorem discovered more than a century ago by Fourier that any periodic phenomenon, however complex, could be represented mathematically by the sum of a number of terms each representing a simple harmonic oscillation of the varying property in question. The proof of this theorem can be obtained in any of the standard works on mathematical analysis. We will give a few simple illustrations here.

The simplest illustration of a pure harmonic movement is the motion of a point backwards and forwards along the diameter of a circle, provided the point is the projection on the diameter of another point which is travelling *uniformly* round the circumference of a circle. Calling the centre of the circle O, the point on the diameter P and that on the circumference Q, we can write

$$x = a \cos 2\pi w,$$

where $x = OP$, $a =$ radius of the circle and $2\pi w = \angle POQ$. Obviously w increases uniformly with the time and we can write

$$w = \omega t + \delta,$$

where ω is the frequency or number of oscillations of P (*i.e.* rotations of $\overline{OQ}$) per second and δ is an arbitrary constant angle. It is customary to refer to w as an "angle variable". The term does not so much imply that w is an angle as that it is a variable which is a *linear* function of the time. It will appear presently that cases arise in which the "angle variables" are not angles, and in which angles that might be used as co-ordinates to define the configuration of a system, are not angle variables because they do not alter uniformly with the time. The important point to observe about this simple illustration is that the behaviour of a co-ordinate x which does not vary uniformly with the time is expressed by means of a variable w which does do so. Now what Fourier was able to show is that whatever be the nature of a vibratory motion executed by P to and fro along a line through O, it could be represented by the sum of a series such as that on the right-hand side of this equation—

$$x = a \cos 2\pi(w + \delta) + a' \cos 2\pi(2w + \delta') + a'' \cos 2\pi(3w + \delta'') + \text{etc.} \quad (6)$$

In this w is once more an angle variable given by

$$w = \omega t,$$

where ω is the fundamental Fourier frequency. The result of Fourier's analysis of a complex vibratory motion as stated thus shows that it is the resultant of a number of simple harmonic oscillations each with a definite amplitude (a, a' , etc.) and each having one of the series of harmonic quantities $\omega, 2\omega, 3\omega$, etc., as its frequency. The quantities δ, δ' ,

δ ", etc., are usually called "epochs" and serve to define at what moments each simple vibration attains a definite phase. Thus in the fundamental vibration the displacement clearly attains its maximum positive value (*i.e.* a) at times given by

$$t = -\delta, \quad t = \frac{1-\delta}{\omega}, \quad t = \frac{2-\delta}{\omega}, \text{ etc.}$$

Theoretically the number of simple harmonic terms is in general infinite, but in practice the number is limited by the fact that beyond a certain term the amplitudes become negligible. Thus in the analysis of the tidal oscillations of the estuary of the Mersey about forty terms are used.

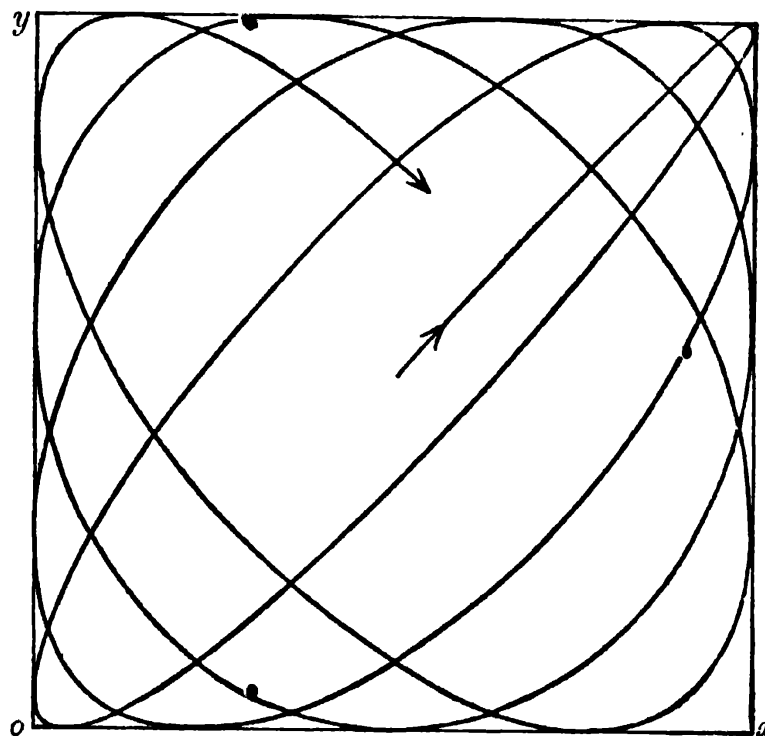


FIG. 22.—(From N. Campbell's *Modern Electrical Theory*, Supplementary Chap. XV., "Series Spectra," Cambridge University Press, 1921.)

This illustration concerns a case where there is only one degree of freedom. We can easily extend it to two degrees or three. Thus taking x and y to represent Cartesian co-ordinates of a point we can write

$$\left. \begin{aligned} x &= a \cos 2\pi(w_1 t + \delta_1) \\ y &= b \cos 2\pi(w_2 t + \delta_2) \end{aligned} \right\} \quad (7)$$

where $w_1 = \omega_1 t$ and $w_2 = \omega_2 t$ are two angle variables. We are now following the oscillations of a point P in a plane by studying the two projections on the axes. In general, if ω_1 and ω_2 are incommensurate (*i.e.* their ratio cannot be represented exactly as the ratio of two integers), the path of the point never returns on itself. It fills up closely all the space inside the rectangle $x = \pm a, y = \pm b$ (as in Fig. 22), meaning

that, having assigned arbitrarily the position of a point in the diagram, the path will, after a sufficient lapse of time, pass as close as we like to this point. If however, ω_1 and ω_2 are commensurate, *i.e.* are integral multiples of a common factor, the path is closed; and we have what is commonly called in quantum theory a "degenerate case". In particular, if $\omega_1 = \omega_2$, the path becomes an ellipse touching the sides of the rectangle. If in addition $\delta_1 = \delta_2$, the path becomes a diagonal of the rectangle. If $a = b$, and $\delta_1 - \delta_2 = \frac{\pi}{2}$, the path is circular.

For the case of three degrees of freedom we introduce three co-ordinates and write

$$\left. \begin{aligned} x &= a \cos 2\pi(w_1 + \delta_1) \\ y &= b \cos 2\pi(w_2 + \delta_2) \\ z &= c \cos 2\pi(w_3 + \delta_3) \end{aligned} \right\} \quad (8)$$

where $w_1 = \omega_1 t$, $w_2 = \omega_2 t$, $w_3 = \omega_3 t$ are three angle variable. In general, the path is unclosed, filling up closely the volume within the rectangular parallelepiped $x = \pm a$, $y = \pm b$, $z = \pm c$. If, however, two of the frequencies are commensurate, or if a relation such as

$$l\omega_1 + m\omega_2 + n\omega_3 = 0,$$

where l, m, n are integers (positive or negative) is true, then the motion is "singly degenerate"; the path is still unclosed but does not fill up the whole volume; it merely fills up the area of some two dimensional surfaces, which touches the faces of the parallelepiped. *E.g.*, if $\omega_1 = \omega_2$, but ω_3 is incommensurate with either, the path winds back and forth, never returning on itself, on the surface of an elliptic cylinder with the axis of z as axis. If two relations, such as the above, exist, *i.e.* if all three frequencies are commensurate, the movement is "doubly degenerate" and the path returns on itself after a finite number of spirals, and does not fill up even a superficial extension.

If the oscillation with three degrees of freedom is not simply harmonic in each component, we can as before analyse each component and write—

$$\left. \begin{aligned} x &= a \cos 2\pi(\omega_1 t + \delta_1) + a' \cos 2\pi(2\omega_1 t + \delta_1') + a'' \cos 2\pi(3\omega_1 t + \delta_1'') + \text{etc.} \\ y &= b \cos 2\pi(\omega_2 t + \delta_2) + b' \cos 2\pi(2\omega_2 t + \delta_2') + b'' \cos 2\pi(3\omega_2 t + \delta_2'') \\ z &= c \cos 2\pi(\omega_3 t + \delta_3) + c' \cos 2\pi(2\omega_3 t + \delta_3') + c'' \cos 2\pi(3\omega_3 t + \delta_3'') \end{aligned} \right\} \quad (9)$$

We proceed to a further generalisation in the analysis of vibratory motion and to do this we reconsider the case of a simple vibratory motion along a straight line through the origin, the line itself, however, turning in the plane OXY with a uniform angular velocity (Fig. 23).

Let w_1 be the angle variable for the simple harmonic motion so that $w_1 = \omega_1 t$; let ω_2 be the frequency of revolution of the rotating line; then the polar co-ordinates of the point at time t are

$$\left. \begin{aligned} r &= a \cos 2\pi(w_1 + \delta_1) \\ \theta &= 2\pi(\omega_2 t + \delta_2) = 2\pi(w_2 + \delta_2), \end{aligned} \right\}$$

where a is the amplitude of the harmonic oscillation, and δ_1 and δ_2 are arbitrary epoch angles.

The Cartesian co-ordinates are given by

$$\begin{aligned}x &= r \cos \theta = a \cos 2\pi(w_1 + \delta_1) \cos 2\pi(w_2 + \delta_2) \\y &= r \sin \theta = a \cos 2\pi(w_1 + \delta_1) \sin 2\pi(w_2 + \delta_2)\end{aligned}$$

or

$$\begin{aligned}x &= \frac{1}{2}a \cos 2\pi(w_1 + w_2 + \delta_1 + \delta_2) + \frac{1}{2}a \cos 2\pi(w_1 - w_2 + \delta_1 - \delta_2) \\y &= \frac{1}{2}a \sin 2\pi(w_1 + w_2 + \delta_1 + \delta_2) - \frac{1}{2}a \sin 2\pi(w_1 - w_2 + \delta_1 - \delta_2) \\&= \frac{1}{2}a \cos 2\pi(w_1 + w_2 + \delta_1 + \delta_2 - \frac{1}{2}) + \frac{1}{2}a \cos 2\pi(w_1 - w_2 + \delta_1 - \delta_2 + \frac{1}{2})\end{aligned}$$

which can be written—

$$\begin{aligned}x &= \frac{1}{2}a \cos 2\pi(w_1 + w_2 + \epsilon) + \frac{1}{2}a \cos 2\pi(w_1 - w_2 + \epsilon') \\y &= \frac{1}{2}a \cos 2\pi(w_1 + w_2 + \epsilon'') + \frac{1}{2}a \cos 2\pi(w_1 - w_2 + \epsilon''')\end{aligned} \quad (10)$$

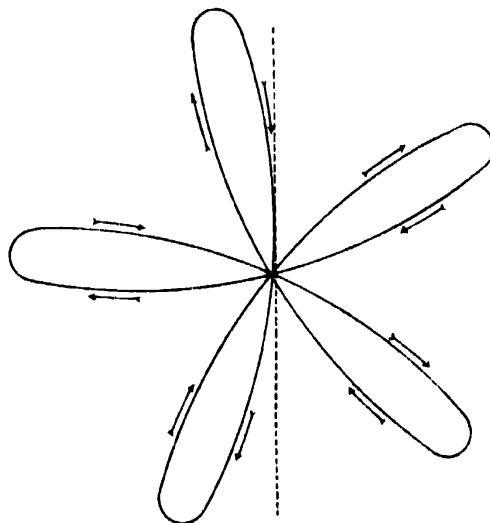


FIG. 23.

The figure (Fig. 23) described in this case is a rosette shaped figure which returns on itself after a finite number of loops if ω_1 and ω_2 are commensurate; it does not do so, but fills up closely the area within the circle $r = a$, if ω_1 and ω_2 are incommensurate. The difference between (7) and (10) is obvious at a glance. Further, if the vibrations along the rotating line were compounded of many simple harmonic vibrations so that r would be equal to the right-hand side of (6), then instead of (10) we should have x and y equal individually to the sums of such terms as

$$a_p \cos 2\pi(pw_1 \pm w_2 + \epsilon),$$

where p is integral. Finally, if the rotation of the line were not at a uniform rate, we could not equate θ to an angle variable; but as $\cos \theta$ and $\sin \theta$ are periodic functions of θ , returning to their former values after an increase of 2π in θ , we could expand them as Fourier series of the angle variable w_2 , where $w_2 = \omega_2 t$, ω_2 being the average frequency

of rotation over a long period of time. On considering the result of multiplying a series expression for r in terms of w_1 by a series expression for $\cos \theta$ or $\sin \theta$ in terms of w_2 , the reader will realise after a little thought and pencil work that x and y each become series expressions, such as

$$\begin{aligned} x &= \sum a_{pq} \cos 2\pi(pw_1 + qw_2 + \delta_{pq}) \\ y &= \sum b_{pq} \cos 2\pi(pw_1 + qw_2 + \epsilon_{pq}) \end{aligned} \quad (11)$$

Here p and q are integers which may theoretically have any values between $-\infty$ and $+\infty$, and there are theoretically as many terms as there are ways of choosing a pair of integers from all negative and positive integers. a_{pq} and b_{pq} are amplitudes for a particular term and δ_{pq} and ϵ_{pq} epochs. In practice, a limited number of terms are sufficient to give reasonable accuracy.

The extension to three dimensions is obvious. The most general expression for the vibratory motion of a single point in space is given by

$$\begin{aligned} x &= \sum a_{pqs} \cos 2\pi(pw_1 + qw_2 + sw_3 + \delta_{pqs}) \\ y &= \sum b_{pqs} \cos 2\pi(pw_1 + qw_2 + sw_3 + \epsilon_{pqs}) \\ z &= \sum c_{pqs} \cos 2\pi(pw_1 + qw_2 + sw_3 + \zeta_{pqs}) \end{aligned} \quad (12)$$

Here p, q, s are a triplet of three integers (positive or negative), the a, b, c symbols are amplitudes, the δ, ϵ, ζ symbols are epochs; w_1, w_2, w_3 are angle variables, *i.e.*, $\omega_1 t, \omega_2 t, \omega_3 t$ where $\omega_1, \omega_2, \omega_3$ are three fundamental frequencies. It should be noted that in cases where the motion is not "degenerate" in the sense referred to above, we must have at least three *distinct* fundamental frequencies, since we have for a moving point three degrees of freedom. If, for instance, ω_1 and ω_2 were commensurate, their common factor would replace them as a single fundamental frequency, or if a relation of the form

$$l\omega_1 + m\omega_2 + n\omega_3 = 0$$

(l, m, n being integers, positive or negative) existed, there would again be only two fundamental frequencies and the path would ultimately only fill up closely a portion of a surface, instead of a volume of space. If two relations of the above form existed there would only be one fundamental frequency and in finite time the path would begin to repeat itself exactly.

Of course it is possible to introduce more angle variables, but the justification of this leads us into general dynamical theory. We must content ourselves by simply stating that if a system has n degrees of freedom, and is not degenerate, there are n fundamental frequencies involved and n angle variables required for the expression of the co-ordinates of any point of the system, which then become individually the sum of terms such as

$$a \cos 2\pi(s_1 w_1 + s_2 w_2 + s_3 w_3 + \dots + s_n w_n + \delta)$$

where $s_1, s_2, s_3, \dots, s_n$ are a set of n integers, a and δ being amplitude

and epoch, in general, different for different terms or for the same term in the series for different co-ordinates.

Before leaving this subject of Fourier analysis it might be as well to refer to it in connection with the types of orbits which occur in connection with atom theory. Under the influence of an inverse square law the unperturbed path of an electron will be in general an ellipse round the nucleus (more precisely round the centre of gravity) as focus. The two most natural co-ordinates for the electron are the polar co-ordinates r , distance of electron from focus, and θ , angle which the radius vector to the electron makes with the major axis. It should be clearly realised that θ could not be an angle variable; it does not alter uniformly with time. But it is not difficult to discover an angle variable; for it is one of Kepler's well-known laws of planetary motion (deducible simply from the fact that the force is directed towards the focus), that if P is the electron, S the focus and A an extremity of the major axis, then the area of the elliptic sector SAP varies directly in proportion to the time. Hence the quotient of the area SAP by the area of the ellipse is the angle variable, for if multiplied by 2π we have an angle which alters uniformly with time and increases by 2π while the radius vector SP varies from its maximum to its minimum value and back once more to its maximum, or while the azimuth θ varies by 2π ; *i.e.* $\cos \theta$ and $\sin \theta$ go through a complete period of their values. In an unperturbed ellipse only this one angle variable is required to describe the oscillatory behaviour of the moving electron. It is a completely degenerate motion, *i.e.* purely periodic as distinct from the "conditionally periodic" motions referred to above, where the path never quite returns on itself but ultimately fills in closely a portion of two-or-three-dimensional space. Now in atom theory it is these conditionally periodic motions which are of extreme interest. We never actually have unperturbed elliptic motion of the electron. By reason of the perturbing effects of other electrons the ellipse is, as it were, rotated slightly from its previous position by the time the electron has travelled round so that we get a path as indicated in the Fig. 24.

Even in the case of the hydrogen atom where there is only one electron, and no other electrons come in to perturb its path, yet on account of the variability of mass with speed, which is a feature of the new Relativity dynamics, there is a slow precession of the axis of the ellipse. (This brilliant suggestion of Sommerfeld has led to a remarkable elucidation of the fine structure of the Balmer lines; *cf.* Appendix IV.) Added to this we frequently have to deal with perturbing effects due to an external electric field (Stark effect) or to an external magnetic field (Zeeman effect) or to the fields of neighbouring atoms (pressure shift). All these produce similar effects on the simple elliptical path. Under such circumstances we must introduce at least two angle variables; we should require a third if the plane of the orbit should also change, but we shall leave that case aside for the moment. It is not difficult to see why two angle variables are required, since the time in which the radius vector r returns to its maximum value (apocentre) is not quite the same

as the period in which the azimuthal angle θ (with a *fixed* line in the plane now) increases by 2π so that $\cos \theta$ and $\sin \theta$ pass through a cycle of values. The value of the frequencies, *viz.* ω , the azimuthal frequency (*i.e.* the number of times per second the azimuth increases by 2π) and ω' the radial frequency (*i.e.* the number of times per second the radius vector goes through a complete cycle of values), are not very different, but some difference there must be unless the motion is to degenerate into a

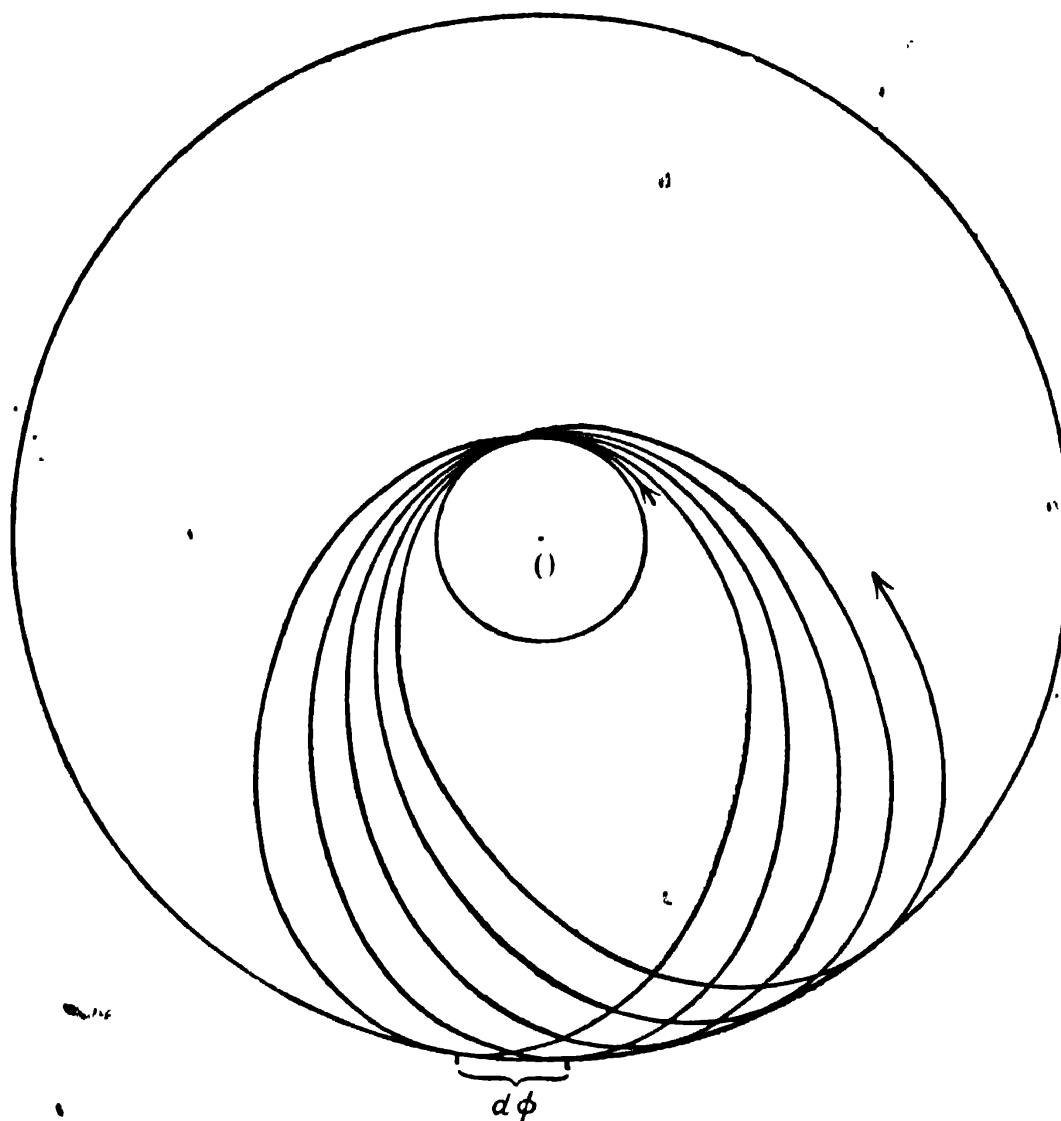


FIG. 24.—(From N. R. Campbell's *Modern Electrical Theory*, Supplementary Chap. XV., Cambridge University Press, 1921.)

purely elliptical movement. The actual mathematical solution of the problem to express the Cartesian co-ordinates x and y of the perturbed electron referred to axes with focus as origin, is not a bit of elementary mathematics; it can be done and the inquisitive can find out by studying a book on "Planetary Theory".

We may state the fact simply thus: for a conditionally periodic motion of an electron in an orbit whose plane is not altering—

$$\begin{aligned} x &= \sum a_{pq} \cos 2\pi(pw + qw' + \delta_{pq}) \\ y &= \sum b_{pq} \cos 2\pi(pw + qw' + \epsilon_{pq}) \end{aligned} \quad (13)$$

Here p and q are integers (positive or negative), a_{pq} and b_{pq} are amplitudes, $w = \omega t$ and $w' = \omega' t$ where ω is the "azimuthal" frequency and ω' is the "radial" frequency.

Returning, after this rather long digression on Fourier analysis, to the Principle of Correspondence we have first to show how to set up a correspondence between a quantum transition from one orbit to another and a Fourier term or simple vibration in (13). Suppose we have an orbit whose *azimuthal* quantum number is n and its *radial* quantum number is n' ; and suppose the leap of the electron is from this orbit to one in which the azimuthal and radial quantum numbers are respectively k and k' . Let—

$$\text{and } \left. \begin{aligned} n - k &= p \\ n' - k' &= q \end{aligned} \right\} p \text{ and } q \text{ may be positive or negative.}$$

then this leap is said to correspond to the terms in the x and y expansions (13) involving the argument $pw + qw'$, i.e. the simple component vibration whose azimuthal "order-number" (*ordnungszahl*) is p or $n - k$ and whose radial order-number is q or $n' - k'$. Such a simple vibration has a Fourier frequency $p\omega + q\omega'$; but, of course, as already emphasised, this is not the frequency of a line in the emitted light on the quantum theory; that would be given by dividing the change in energy after the jump by h . Still for large quantum numbers and small differences p and q , the quantum frequency and Fourier frequency approach one another in value. But classical theory further asserted that these terms in (13) also gave the intensity and polarisation of the light of this Fourier frequency which could be emitted (or absorbed) if this theory were correct. This it did by means of the amplitude coefficients a_{pq} , b_{pq} and the epochs δ_{pq} , ϵ_{pq} . E.g., if b_{pq} were zero, the intensity of the light should be proportional to a_{pq}^2 and it should be polarised at a point Q with the electric vector in the plane OXQ and perpendicular to OQ. If $\delta_{pq} = \epsilon_{pq}$ it would again be linearly polarised with intensity proportional to $a_{pq}^2 + b_{pq}^2$. In general it would be elliptically polarised. Now what the Principle of Correspondence postulates is that this information is still approximately correct for the actual light emitted in quantum jump $n - k = p$, $n' - k' = q$. Presumably this statement is correct in the region of slow vibrations, and Bohr simply suggests that until our body of quantum principles is more fully developed, this extrapolation will be of service. It has, in fact, yielded theoretical results in some cases in remarkably good agreement with experimental observation. There is one difficulty, however, which may have occurred to the reader which we should remove before proceeding. In the above statement of the principle do the a_{pq} , b_{pq} , δ_{pq} , ϵ_{pq} refer to the initial orbit or to the final? To be sure for two orbits with large quantum numbers and small differences the values of these quantities would not seriously vary;

but for moderate quantum numbers and comparable order numbers, the amplitudes and epochs for one orbit might differ seriously from those of the other orbit. The frequencies ω and ω' might differ also in the two cases, but that could not affect questions of intensity and polarisation, and in any case frequency is determined by the quantum rule and not by Fourier terms. The way which Bohr suggests to evade this difficulty is purely tentative (as indeed the Principle itself is). He points out that there are an infinity of orbits *mechanically possible* intermediate to the initial and final quantum orbits considered. They are given by the fact that the "modulus of azimuthal periodicity," of any one of them is equal to—

$$\{n' + \lambda(n - n')\}h,$$

where λ has a value between 0 and 1. The "modulus of radial periodicity" is equal to—

$$\{k' + \lambda(k - k')\}h.$$

These are, of course, not quantum orbits, since the multipliers of h in the above expression *are not integers*. Bohr now suggests that the average of all the a_{pq} for these orbits is what should be used in his rule for polarisation and intensity and similarly for the remaining quantities.

In actual calculations this averaging requires some mathematical dexterity, but the procedure is not so arbitrary as it might seem; for it appears on investigation that the optical frequency given by the quantum jump between the two quantised orbits is equal to the average taken over all the intermediate orbits of the corresponding component mechanical frequency which exists in the motion of the electron when it is resolved into its Fourier constituents.

It may be as well to emphasise the nature of the correspondence principle once more. The frequencies in the radiation from the atom are not the frequencies of the harmonic components of the periodic orbital motion, but there is a correspondence between a quantum frequency and a harmonic component such that if the harmonic component is present in the orbital motion then the corresponding quantum jump is possible; the greater the amplitude of the harmonic component, the more probable becomes the quantum jump and the radiation in question is more intense. Further, the state of polarisation of the emitted radiation is determined by the direction of the linear vibration which constitutes the corresponding mechanical constituent in the orbital movement.

This principle helps to fill a gap which must exist in our information concerning intensity and polarisation so long as the mechanism of radiation is unknown; such mechanism being, on account of the discontinuity involved, totally different from the process envisaged in the classical electrodynamics. Einstein, who was the first to face the result of admitting this discontinuity in a logical fashion, has succeeded in proving the Planck law for full radiation, while forsaking any

appeal to continuous processes, and using only a general thermodynamic law concerning radiation due to Wien, and known as Wien's displacement law. In the course of his analysis Einstein has to introduce certain coefficients which measure the tendency within a given time interval for an atomic system to pass spontaneously and without the aid of external radiation from one of its stationary states to another of lesser energy (*cf.* Chap. V., section entitled "Einstein's use of the generalised Bohr model to deduce the law of Planck".) Such a coefficient (represented by A_{β}^{α}) is defined so that in the time interval dt the probability that an atom will spontaneously pass from a stationary state denoted by α to one denoted by β is $A_{\beta}^{\alpha}dt$. For his particular purpose Einstein requires no special information concerning these coefficients as Wien's displacement law comes to his assistance, but it is clear that these quantities will play a very important part in the development of the mathematical analysis of the Bohr atom. The suggestion of Bohr that the coefficient A_{β}^{α} depends in some way on the average amplitudes of the component of mechanical vibration corresponding to the jump α to β is a first step towards their formulation, but any attempts at determining the functional relationship between A_{β}^{α} and the amplitude are still tentative although they have given encouraging results in one or two important cases. Even if these coefficients, the *a priori* probabilities of definite quantum jumps, were more completely known than they are, the problem of intensity of the corresponding radiation is not yet solved unless account is also taken of the probability that the atomic system is actually in the initial stationary state (the state α). So, altogether, the mathematical physicist has an exceedingly difficult problem to solve. He has in all probability had his feet set in the right road, but it will be rough going.

One or two simple illustrations of the use of the correspondence principle may be given in conclusion.

Consider, for instance, the ideal linear oscillator of Planck with a simple mechanical frequency ω , so that its displacement equation is—

$$x = a \cos 2\pi\omega t.$$

Now, the theory referred to above leads very simply in this case to the calculation of a modulus of periodicity; for the velocity at time t is given in magnitude by $2\pi\omega a \sin 2\pi\omega t$, so that the kinetic energy is $2\pi^2 m \omega^2 a^2 \sin^2 2\pi\omega t$; if this is doubled, multiplied by dt and integrated from 0 to $1/\omega$ we get $2\pi^2 m \omega a^2$ as the modulus. Hence the n th stationary state of the oscillator has an amplitude a_n given by—

$$2\pi^2 m \omega a_n^2 = nh.$$

But the energy of a vibration with this amplitude is—

$$\begin{array}{c} 2\pi^2 m \omega^2 a_n^2 \\ \text{i.e.,} \quad nh\omega. \end{array}$$

In jumping from the state n to the state k the oscillator should therefore emit a radiation whose frequency is—

$$\frac{nh\omega - kh\omega}{h}$$

or

$$(n - k)\omega.$$

That is, the radiation should consist of lines with optical frequencies ω and any integral multiples of ω . Now it is essential in the use which Planck makes of his oscillator in the theory of full radiation that the radiation emitted should be monochromatic and of frequency ω . That was provided for in his work by assumptions involved in his view that absorption should be continuous, emission discontinuous; a view that naturally finds no place in the stationary state hypothesis of Bohr. Is, therefore, Planck's proof of the full radiation formula invalid on Bohr's assumption? By no means. Looking at the equation for the mechanical frequency above we find only one term and that term involving ω ; there are no terms involving 2ω , 3ω , 4ω , etc.; in other words, the amplitudes corresponding to "order numbers" 2, 3, 4, etc., are zero. Hence the probabilities of jumps involving a decrease in the quantum number of 2 or 3 or 4, etc., are also zero. In short, in any jump the quantum number can only alter by unity; and so in the above calculation $n - k$ can only be unity. Thus the validity of Planck's proof is maintained in the new physical theory by the correspondence principle. As a matter of fact, we see it here acting as a selection principle, *i.e.* selecting certain jumps as possible, and ruling out others as impossible. A very notable use of the principle in this way, but one into whose mathematical details we cannot enter, shows why in the hydrogen spectrum, for instance, jumps between certain orbits are ruled out. In fact, if the jump between two orbits involves change more than unity in the *azimuthal* quantum number of an orbit, the correspondence principle when applied in detail rules it out, for it shows that in the harmonic analysis of the orbital motions only the order number unity appears for the azimuthal co-ordinate. (Care must be exercised here not to acquire the idea that this limits the change in the *total* quantum number to unity, a mistake which would reduce the Balmer series, for example, to one line H_{α} .)

This selection of possible jumps plays an important part in the discussion of the intensities of the "fine structure" lines into which each of the lines of hydrogen is analysed by a spectrometer of high resolving power. A similar investigation has proved very successful when applied to the effect of electric and magnetic fields on the structure of the ionised helium lines (Stark and Zeeman effects). But a case which will appeal more readily to readers of this volume is the following.

Observations on the absorption spectra of diatomic gases show that certain strong absorption bands (band heads), which, according to general evidence, can be ascribed to the relative vibratory motion of the

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two atoms, are present unaccompanied by bands whose frequencies are integral multiples of the frequency of this strong one; or if so accompanied, these harmonic bands are but faint. This finds a natural explanation, according to the correspondence principle, in the postulate that the passage of the molecule from a stationary state to a non-successive state is impossible or at all events improbable, because in the harmonic analysis of the relative vibratory motion the amplitudes of all but one term are negligible. But we find a still further application if we consider the "fine structure" of these absorption bands which, in accordance with an idea first propounded by Bjerrum, is now ascribed to rotation of the vibrating molecule around an axis perpendicular to the line joining the two atomic nuclei. Calling the moment of inertia of the molecule about this axis J , we have to quantise this rotatory motion. Let the frequency of the rotation be ω , so that the angular velocity is $2\pi\omega$. The kinetic energy is $\frac{1}{2} J(2\pi\omega)^2$ or $2\pi^2 J\omega^2$; the accumulation of action during one period of rotation is $4\pi^2 J\omega^2 \times 1/\omega$; i.e. the modulus periodicity is $4\pi^2 J\omega$. Hence in the stationary states of rotation, the frequencies of rotation, $\omega_1, \omega_2, \omega_3$, etc., are given by—

$$\begin{aligned} 4\pi^2 J\omega_1 &= h, \\ 4\pi^2 J\omega_2 &= 2h, \\ 4\pi^2 J\omega_3 &= 3h, \\ &\text{etc.} \end{aligned}$$

The energies of rotation in each state, $2\pi^2 J\omega_1^2$ are clearly $A \cdot 1^2, A \cdot 2^2, A \cdot 3^2$, etc., where

$$A = \frac{h^2}{8\pi^2 J}$$

(In this it is assumed that J is the same for each state.)

Let ν denote the frequency of the vibratory motion of the atoms then in the stationary state whose vibration quantum integer is n_v and whose rotation quantum integer is n_r , the total energy (vibrational and rotational combined) is—

$$n_v h\nu + A n_r^2.$$

As we are considering *absorption* we consider the quantum leap to a state of larger *total* energy, whose quantum numbers are k_v and k_r , and whose energy is—

$$k_v h\nu + A k_r^2$$

It should be carefully noted that owing to the preponderating value of the first term in these expressions, k_v must be greater than n_v , if the second state has larger total energy, but that k_r is not necessarily greater than n_r ; in other words, the rotational part of the energy in the second state may be less than in the first. Applying the frequency rule for such a jump the frequency of the absorbed radiation should be—

$$(k_v - n_v)\nu + B(k_r^2 + n_r^2),$$

where

$$B = \frac{A}{h} = \frac{h}{8\pi_2 J}$$

Now by the application of the correspondence principle already made to vibratory motion we assume that only leaps in which n_v changes by unity are possible, so that the lines become—

$$v + B(k_r^2 - n_r^2).$$

Now a similar restriction is put on the rotation quantum jumps; for a glance back to the analysis of the earlier part of this appendix will remind the reader that the imposition of a rotation of frequency ω on a system introduces in the Fourier analysis of the movement an expression $\pm 2\pi\omega t$ into the sum of multiples of the angle variables which occurs after the cosine in any of the Fourier terms. Now by the principle this implies that any possible jump will only allow the corresponding quantum number to change by plus or minus unity. (We barred out the possibility of a change of minus unity in the vibration quantum number, as this would lead to a negative frequency.) As a consequence, $k_r = n_r \pm 1$, and so a whole host of lines apparently possible on an elementary quantum view are ruled out and the following selected—

$$v \pm \alpha B,$$

where α is any *odd* integer.

Observation of the “rotation-vibration” spectrum of HCl gives remarkably good support to this conclusion. (It so happens that the line $v + B$ is actually missing. This, however, does not arise as a conclusion from the correspondence principle. Its explanation depends in all probability on the fact—revealed by this gap in the line spectrum—that the state of the molecule in which there is neither vibration nor rotation is extremely improbable.)

APPENDIX VI.

MOLECULAR ROTATIONS AND INFRA-RED ABSORPTION SPECTRA OF GASES.

(Cf. Kratzer, *Zeitsch. Physik*, **3**, 289 (1920)).

THIS subject has been discussed up to a certain point in the section of Chap. V., "Infra-red absorption spectra of gases". We have there considered the change in the molecular motion from a state denoted by (n, m) to a state (n', m') where n (or n') is the quantum number characterising the vibrational energy of the atoms in the Bohr sense, and m (or m') refers to the quantum number of the rotational state of the molecule. If the change considered gives rise to the absorption of one quantum of energy of frequency $\nu_{m, m'}^{n, n'}$, this frequency may be found by equating the quantum $h\nu_{m, m'}^{n, n'}$ to the difference in the two energy contents of the molecule in the two states, thereby giving—

$$\nu_{m, m'}^{n, n'} = \nu_0(n' - n) + \frac{h}{8\pi^2 I}(m'^2 - m^2) \quad (1)$$

The quantities represented by n, n', m, m' , are integers, and up to this point we have regarded any combination of numbers as permissible. To account for the whole of the observed facts, however, notably for the absence of the central absorption sub-band itself and also for the next sub-band on *one* side of this central position in the (approximately) symmetrical broad band (which is composed of many sub-bands), Kratzer has introduced the important limitation that all numerical combinations of the two (rotational) integers m and m' are not permissible. In order to determine the physically possible transitions of the molecule from one rotational state¹ to another use may be made of Bohr's Principle of Correspondence (cf. Appendix V.).

On the basis of this principle as applied to the present case we have seen all transitions are excluded except those involving unit change in the integer m .

• Bearing this in mind equation (1) may be written—

$$\nu_{m, m \pm 1}^{n, n'} = \nu_0(n' - n) + \frac{h}{8\pi^2 I}(m^2 - (m \pm 1)^2) \quad (1a)$$

0, 1, 2, 3, etc.;

¹ Since the moment of inertia I of the molecule is regarded as constant, or practically so, we cannot speak of different rotational orbits in the same sense as Bohr electronic orbits. Rotational states are assumed to differ from one another (discontinuously) in respect of speed of revolution of the molecule.

with the restriction that $m = 1$ is excluded when $m = 0$, since only positive values of the quantum number are contemplated in equation (1). We would expect therefore a series of narrow absorption sub-bands in the near infra-red with a common frequency difference $h/4\pi^2 I$, grouped on either side of a central frequency $\nu_{0,0}^{n,n'} = \nu_0(n' - n)$ thus—



Comparison with experiment, especially in the case of the halogen hydracids, shows that the predicted series is justified as regards the general grouping, but that experimentally two sub-bands are missing in the absorption spectrum, namely those corresponding to $\nu_{0,0}$ and $\nu_{0,1}$. The sub-band $\nu_{0,0}$ would be given by a change in the energy (and consequently the frequency) of atomic vibration in a rotationless molecule, and its absence would point to a very small probability of existence of the zero state of rotation. The available evidence in the field of molecular heats of gases seems to point to the same conclusion (*cf.* Reiche, *Ann. Physik*, **58**, 657, 1919). If we admit the improbability of existence of the rotationless molecular state, however, it would also appear necessary to exclude the possibility of the changes $0 \rightleftharpoons 1$, and the two sub-bands corresponding to these transitions should be absent from the observed absorption spectra in addition to the $\nu_{0,0}$ frequency. Actually, however, only one of these sub-bands is absent, namely that corresponding to the $0 \rightarrow 1$ transition, the transition $1 \rightarrow 0$ being observable. (NOTE.—The change from 0 to 1 is clearly one involving absorption of energy. The rotational term in equation (1) is therefore added arithmetically to the vibrational term, thus giving a frequency which is greater than that of the central position itself. That is, not only is the central sub-band itself missing but also the next sub-band on the short wave side of the central position.) To explain the apparent discrepancy Kratzer assumes that the zero rotational state is by no means an *impossible* state. The evidence of specific heats and the absence of the frequency $\nu_{0,0}$ merely indicate that the *life* of the rotationless state is vanishingly small, asserting nothing as to the possibility of its occurrence. It is conceivable that the rotationless state could be produced under the influence of a radiational field, but only exist for a very short time and be changed by any extraneous circumstance into a more probable state. Note that it is thereby assumed that the act of absorption is not determined by the *life* of the molecule in the *end* or *second state* of the transition which accompanies the absorption. On the other hand, it might reasonably be expected that the radiation must act on the molecule in its *initial state* for a finite time in order that absorption may take place. A finite statistical probability is therefore required for the initial state. This condition is fulfilled for the $m = 1$ state of rotation, but not for the zero state, and hence the absorption sub-band corresponding to the transition $1 \rightarrow 0$ will appear, whilst that corresponding to the

reverse change $0 \rightarrow 1$ will be absent. From a similar line of reasoning applied to the case of emission Kratzer concludes that here the reverse effect will take place, *i.e.* the emission sub-band $1 \rightarrow 0$ will not appear.

In addition to the apparent anomaly just discussed between the predicted and the experimentally observed number of sub-bands constituting the complex short infra-red band, a further discrepancy occurs in connection with the spacing of the absorption maxima. According to the simple theory, expressed in equations (1) and (1a) above, the maxima should be equidistant from one another. Actually a slight asymmetry is observed in the grouping about the central position in the case of HF, HCl, and HBr as already pointed out in Chap. IV. The bands tend to crowd together towards the short wave end of the spectrum. To explain this asymmetry Kratzer considers that the atoms in such a dipole as HCl do not behave as simple harmonic oscillators, *i.e.* the restoring force is not exactly proportional to the displacement. This will affect not only the term expressing vibrational energy but also the moment of inertia of the molecule on which the rotational term depends. On the basis of a more general law of force Kratzer has calculated corrected positions of the absorption maxima which are in excellent agreement with the positions observed for the three gases mentioned.

It is to be remembered that the whole of the above considerations refer to the structure of the absorption band in the short infra-red region, this band being compounded of atomic vibrational motion along with molecular rotational terms. The individual rotational bands themselves apart from atomic vibration should in general be observable, but naturally only in the very far infra-red. In this region, which has not yet been examined sufficiently, there should be one missing line corresponding to the change from rotationless state to $m = 1$, since the rotationless state is fugitive. Naturally in this far infra-red region we cannot expect to find in the absorption spectrum any bands corresponding to changes from higher values of m to lower values since such transitions by themselves would mean emission and not absorption. The longest rotational band on the above basis giving rise to absorption should correspond with the change $m = 1$ to $m = 2$, *i.e.* the frequency of the starting band of the series in this region due solely to rotation should be $3h/8\pi^2 I$. This conclusion should be verifiable experimentally in the case of gaseous halogen hydrides: at present (1923) experimental data are insufficient. In the case of water vapour the value of $3h/8\pi^2 I$ would correspond to a wave-length 115.6μ which is by no means the longest wave-length actually observed by Rubens (*cf.* section on the infra-red absorption spectra of gases in Chap. V.). It must be remembered, however, that the H_2O molecule has two unequal moments of inertia and consequently equation (1) employed above is inadequate.

Note on Molecular Precession.

In the foregoing section the type of molecular motion dealt with has been rotation around an axis which is perpendicular to the line

joining the two atomic nuclei in the case of a diatomic gas molecule (cf. Chap. I., Fig. 3*b*), and it has been tacitly assumed that the molecule possesses no intrinsic spin round the nuclear axis itself. Krüger, however, has pointed out (*Ann. Phys.*, **50**, 346; **51**, 450, 1916) that such a spin, if it really existed, would give to the molecule the properties of a small gyroscope, free of course from gravitational influence. Incidentally the pure translational motion of such molecules is the same whether the molecules possess gyroscopic properties or not, *i.e.* the translational energy corresponds to the familiar three degrees of freedom. But at least two additional degrees of freedom must exist to account for the magnitude of the specific heats of diatomic gases. These additional degrees of freedom have been ascribed, in the first place, by Bjerrum to simple rotation of the molecule as a whole, the axis of rotation being necessarily perpendicular to the figure axis or line joining the nuclei. However, the fundamental equations of gyroscopic motion show that a gyroscope cannot carry out any rotations, but it can be put into a state of oscillatory motion which, in the case of a symmetrical gyroscope free from external forces, corresponds to a regular precession. This type of motion called by Krüger precessional vibration is that illustrated in Chap. I., Fig. 3*d*. It would be more correct perhaps to call such motion, Poincot motion.

Gyroscopic motion would be conceivable if the electrons in a molecule were arranged in rings, each ring containing several electrons. This was in fact the kind of model envisaged in the older theories of atomic structure.¹ The more recent views of Bohr (dealt with in Chap. V.) deny the existence of such rings of electrons, and on this basis therefore it would seem improbable that rotation *round* the axis joining the nuclei would occur.

There is other evidence pointing to the absence of angular momentum round the axis joining the nuclei in such diatomic gas molecules as H_2 and N_2 . If motion of the gyroscopic type occurred it would indicate a structure which would be expected to exhibit magnetic properties. The absence, however, of the Zeeman effect in the band spectrum of hydrogen (which spectrum is attributed to the molecule as distinct from the atom) shows that the molecule does not possess any magnetic moment round this axis. In the same way the characteristics of the "cyanogen" band spectrum ascribed now to the nitrogen molecule would again point to the absence of angular momentum round the figure axis, *i.e.* the line joining the nuclei. The state of zero angular velocity around this axis would seem to be at least the most probable and perhaps the only possible condition of these and other diatomic gas molecules.

¹ Even granting such a structure, say to the HCl molecule, it can be shown that on quantising the precessions an expression is obtained similar in form to that obtained on the basis of rotations, but at the same time this equation cannot be reconciled with observations since the calculated separation of the sub-maxima or narrow bands (which together constitute the known broad absorption band in the short infra-red) works out considerably greater than the observed separation (cf. Reiche, *Zeitsch. Physik*, **1**, 283, 1920).

APPENDIX VII.

EINSTEIN'S LAW OF THE PHOTOCHEMICAL EQUIVALENT.

By R. O. GRIFFITH.

THE object of this appendix is to present the results of experimental work carried out mainly during the past decade, which may serve as a test of what is known as Einstein's Law of the Photochemical Equivalent or the Law of Photochemical Equivalence.

This generalisation introduced in 1912 (Einstein, *Ann. Physik* [iv.], **37**, 832, 1912; also *ibid.* [iv.], **17**, 132, 1905) is usually stated in a form equivalent to the following: If a photosensitive system is subjected to light of frequency ν , the number of molecules (N) of the absorbing substance (photolyte) which decompose, is equal to $Q/h\nu$, where Q is the radiant energy absorbed and h is the Planck constant, or more simply, for each quantum of energy absorbed one molecule of the absorbing substance disappears. It is unnecessary for our purpose to present Einstein's method of derivation of the law; we may simply regard it as founded on the theory of quantum absorption of energy. It will be convenient, in describing much of the experimental work dealing with the law, to use the following notation which is due to Warburg (*Zeitsch. Elektrochem.*, **26**, 54, 1920).

For any photochemical process which occurs under the influence of monochromatic light of frequency ν (wave-length λ), Einstein's law enables us to calculate the value (p) of the quotient

$$\frac{\text{gram-molecules of substance decomposed}}{\text{gram-calories of radiation absorbed}}$$

The energy which must be absorbed in order that one gram-molecule of the photolyte should decompose is $N_0 h\nu$ ergs, where N_0 is the Avogadro constant or $N_0 h\nu / 4.186 \times 10^7$ cals. Substituting the values $N_0 = 6.062 \times 10^{23}$, $h = 6.547 \times 10^{-27}$ ergs/sec., this amount of energy is equal to 9.481×10^{-11} cals., and placing $\nu = c/\lambda$, and expressing λ in microns (μ), the energy in cals. which must be absorbed to decompose one gram-molecule is found to be $28,443/\lambda$ cals.

$$\text{Therefore, } p = \frac{\text{gram-molecules decomposed}}{\text{calories absorbed}} = \lambda/28,443.$$

According to Einstein's law therefore, the extent of photochemical decomposition is proportional to the product of the absorbed radiant

energy and its wave-length, and is independent of all other factors such as temperature. Further, for all photochemical processes, the quantity p has the same value for identical wave-lengths of the light employed. Table I. (Warburg, *loc. cit.*) gives the value of p at various wave-lengths and of its reciprocal, the number of gram-calories of radiation absorbed when one gram-molecule of photolyte decomposes.

TABLE I.

$\lambda(\mu).$	$p \cdot 10^5$ moles. cals.	$\frac{1 \text{ cal.}}{p \text{ moles.}}$
0.207	0.7286	137,300
0.253	0.8904	112,300
0.282	0.9924	100,800
0.486	1.710	58,470
0.589	2.073	48,240
0.800	2.816	35,510

Let us now denote by ϕ the value of the quotient

$$\frac{\text{gram-molecules of photolyte decomposed}}{\text{calories of radiation absorbed}}$$

obtained *experimentally* in any process effected by monochromatic light. If Einstein's law holds for the reaction, then the value of ϕ will be equal to that of p for the given wave-length.

It will be at once evident, however, that Einstein's law *as formulated above* cannot be generally true for actual photochemical processes. This follows on recalling the fact that most photochemical processes are complicated ones involving secondary reactions, *i.e.* thermal reactions subsequent to the actual primary process caused by the light. If these secondary or "dark" reactions involve molecules of the photolyte as reactants or resultants, it is evident that Einstein's law cannot, except by accident, predict the correct result. We must therefore limit the applicability of the law to the primary process; the actually observed amount of chemical action which results from this process may be exactly equivalent to it, it may be some simple multiple, *e.g.* twice or thrice, or it may be much larger or much smaller, depending on the nature and extent of the secondary processes. If in any particular case we know the nature of the primary process and can calculate the velocity of the "dark" reactions which follow, then Einstein's law will enable us to predict quantitatively the net result of illumination. Our present knowledge, however, does not suffice to enable us to effect this, in fact the exact nature of the primary process is unknown. All that it is possible to do at present, therefore, is to measure ϕ for the given reaction, compare this value with the corresponding value of p , and make as plausible hypotheses as possible to account for the observed results.

We may anticipate the results of this comparison by stating that it now appears to be well established that the absorbing molecule absorbs

energy in quanta, and that if we limit Einstein's law to this statement of the process of absorption, it is valid, but it is not in general true if stated in the form given to it earlier. Further, either the absorbing process is accompanied by a simultaneous dissociation of the molecule or there results a modification containing excess energy and which has a higher chemical reactivity than the original molecule. What afterwards follows is determined by the nature of the system, its temperature and pressure in the manner treated by chemical kinetics. The activated molecules may spontaneously dissociate, they may react by collision either with others of different kind or with non-activated molecules of the same kind, they may transfer their excess energy to other molecules, etc. Thus it will happen that many photochemical processes are the resultant effect of several reactions and will show no simple relationship between the number of quanta absorbed and the number of molecules which disappear. In such reactions the value of this ratio will be expected to vary with slight changes in the experimental conditions, e.g. changes in concentration and temperature. In other processes of not so complicated a type simple relationships may be found and we have then to interpret the results in the light of possible primary and secondary reactions.

Most of the experimental work in photochemistry prior to 1913 is not suited to serve as a test of Einstein's law, although in certain cases approximate conclusions may be arrived at, as was shown by Bodenstein who summarised the results of such work in an important paper (*Zeitsch. physikal. Chem.*, **85**, 333, 1913). He divided photochemical reactions into two classes, in the first of which the number of quanta absorbed is apparently nearly equal to the number of molecules decomposed, while in the second the extent of photochemical action is much smaller or (more frequently) much greater than would be anticipated according to Einstein's law.¹ Since then measurements of greater accuracy and suitability for our purpose have been carried out. Any such determination requires (a) a measurement of the extent of photochemical change, (b) a determination of the amount of radiant energy absorbed, not necessarily by the whole system but by the photosensitive substance, (c) that the light employed should be as nearly monochromatic as possible in order that the value taken for ν shall not be seriously in error. In addition, experiments using different wave-lengths should be undertaken, since it is important to determine whether, as postulated by Einstein's law, the value of ϕ is proportional to that of λ . The chief investigations in this field are those of Warburg, who carried out between 1911 and 1919 a series of careful measurements of the rates of photochemical processes in gaseous and liquid systems; more recently, Nernst and his co-workers have undertaken such work and succeeded in finding reactions in which Einstein's law is followed. Tables II. and III. contain a list of the more important of the reactions studied by them and by others,

¹ An account in English of Bodenstein's paper is given in Lind's *The Chemical Effects of Alpha Particles*, Chap. X., *American Chem. Soc. Monographs*.

TABLE II.
GASEOUS SYSTEMS.

Reaction.	Observer.	λ (μ).	$\phi \cdot 10^5$.	$p \cdot 10^5$.	λ (μ).	$\phi \cdot 10^5$.	$p \cdot 10^5$.	λ (μ).	$\phi \cdot 10^5$.	$p \cdot 10^5$.
$2\text{HBr} \rightarrow \text{H}_2 + \text{Br}_2$	Warburg	0'207	1'53	0'73	0'253	1'79	0'89	—	—	—
$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$		"	1'44	"	"	1'85	"	0'282	2'08	0'99
$3\text{O}_2 \rightarrow 2\text{O}_3$ (pressure 125 atmosphere)		"	2'09	"	"	1'55	"	—	—	—
$3\text{O}_2 \rightarrow 2\text{O}_3$ (pressure 300 atmosphere)		"	1'70	"	"	0'83	"	—	—	—
$2\text{O}_3 \rightarrow 3\text{O}_2$ (in helium)		—	—	—	"	1'52	"	—	—	—
$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$		0'207	0'17	0'73	—	—	—	—	—	—
$\text{C}_6\text{H}_{12} + \text{Br}_2 \rightarrow \text{C}_6\text{H}_{11}\text{Br} + \text{HBr}$.	(Nernst, Pusch	0'476	1'79	1'67	—	—	—	—	—	—
	(Nernst, Noddack	0'469	1'65	1'65	—	—	—	—	—	—
$2\text{O}_3 \cdot \cdot 3\text{O}_2$ (sensitised by chlorine)	Bonhoffer	0'416	2'97	*	—	—	—	—	—	—
$2\text{O}_3 \cdot \cdot 3\text{O}_2$ (sensitised by bromine)		0'416	45'4	*	—	—	—	—	—	—

* In these sensitised reactions, the absorbing substance is the halogen, the concentration of which remains unchanged. The values of ϕ refer to gram-molecules of ozone decomposed per calorie absorbed by the halogen.

TABLE III.
LIQUID SYSTEMS.

Reaction.	Observer.	λ (μ)	$\phi \cdot 10^5$	$p \cdot 10^5$	λ (μ)	$\phi \cdot 10^5$	$p \cdot 10^5$	λ (μ)	$\phi \cdot 10^5$	$p \cdot 10^5$
(a) In carbon tetrachloride solution :—										
$2\text{CCl}_3\text{Br} + \text{Cl}_2 \rightarrow 2\text{CCl}_4 + \text{Br}_2$	Nernst, Noddack	0'410	1'34	1'44	0'449	1'42	1'58	—	—	—
$2\text{ClO}_2 \rightarrow \text{Cl}_2 + 2\text{O}_2$	Bowen	0'445	1'28	1'56	—	—	—	—	—	—
$2\text{Cl}_2\text{O} \rightarrow 2\text{Cl}_2 + \text{O}_2$			1'37		—	—	—	—	—	—
(b) In aqueous solution :—										
$2\text{KNO}_3 \rightarrow 2\text{KNO}_2 + \text{O}_2$	Warburg		0'18	0'73	0'253	0'15	0'89	0'282	0'024	0'99
Malic acid $\rightarrow$ fumaric acid			0'02		"	0'038	"	"	0'032	"
Fumaric acid $\rightarrow$ maleic acid			0'08		"	0'087	"	"	0'133	"
$\text{PtCl}_2(\text{OH})_2\text{H}_2 + 3\text{H}_2\text{O} \rightarrow \text{PtCl}(\text{OH})_3\text{H}_2 + 3\text{HCl}$	Boll	0'238	3'52	0'83	0'254	1'66	0'82	0'310	0'101	1'08
$2\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_3 \rightarrow 2\text{CoC}_2\text{O}_4 + 3\text{K}_2\text{C}_2\text{O}_4 + 2\text{CO}_2$	Vranek	0'366	1'90	1'28	0'405	1'25	1'42	0'436	0'881	1'53
$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	Henri and Wurmser	0'230	4'02	0'805	0'256	3'86	0'895	0'280	3'88	0'99
	Kornfeld	0'311	Values of $\phi \cdot 10^5$ vary between 87'2 and 7'6							

Note.—In all the reactions occurring in aqueous solution the value of ϕ is dependent on the concentration of photolyte. The value given above relate in each case (excepting that studied by Kornfeld) to a concentration for which experiments at different wave-length were carried out.

and also indicate the nature of the results obtained. The reactions are here classified according to the nature of the phase, gaseous or liquid, in which they were carried out. In the tables the first column gives the nature of the photochemical change measured, the second the observer, and the remainder the wave-length, of the light employed (λ) and the values of ϕ , *i.e.*

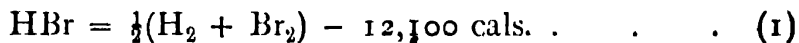
$$\frac{\text{gram-molecules of absorbing substance decomposed}}{\text{calories of radiation absorbed}}$$

and of p for the corresponding wave-length. The latter, as previously explained are calculated from the equation, $p = \lambda/28,443$.

An inspection of these tables shows that in only a few cases is the value of ϕ equal to that of p , although in many the two are not greatly different. In the photochemical decomposition of hydriodic and hydrobromic acids the value of ϕ is almost exactly double that of p at all wave-lengths. Many of the reactions exhibit the discrepancy that an increase in the wave-length of the light employed causes a diminution in the value of ϕ instead of an increase, and it is also seen that in all reactions so far studied in aqueous solution no simple relation between ϕ and p is observed. Before dealing further with these effects, it will be convenient to discuss the results obtained and the mechanisms proposed for reactions 1 to 4 of Table II., after which the remaining reactions will be considered.

The Photochemical Decomposition of Hydrobromic and Hydriodic Acids.

The first reaction in Table II. is the photolysis of gaseous HBr. On exposure to ultra-violet radiation this gas decomposes into hydrogen and bromine, the reaction being expressed by the equation—

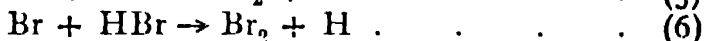
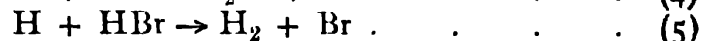


The decomposition was effected by Warburg (*Sitzungsber. Preuss. Akad.*, 1916, p. 314) by diluting the gas either with hydrogen or nitrogen, sweeping the mixture through a quartz cell exposed to monochromatic ultra-violet light into a solution of potassium iodide, where the bromine formed liberated an equivalent amount of iodine which was estimated by titration with thiosulphate solution. The absolute amount of light energy absorbed was determined by a bolometer. Experiments using two wave-lengths 0.209μ and 0.252μ were carried out and the partial pressure of the hydrobromic acid gas was varied. Employing light of 0.209μ the value of ϕ was found to be 1.53×10^{-5} moles HBr decomposed/cal. absorbed, and was the same using either hydrogen or nitrogen as the diluent. At the longer wave-length ϕ was found to be 1.79×10^{-5} . These values are nearly exactly double the values of p for these wave-lengths (0.73×10^{-5} and 0.89×10^{-5}), showing that two molecules are decomposed per quantum absorbed. If one assumes that

the primary process effected by the light is the decomposition of hydrobromic acid into atomic hydrogen and bromine,



there is then the possibility of the secondary process (3), (4), (5) and (6) occurring—



A thermal reaction, however, can only occur if accompanied by a decrease in free energy. This condition is obviously satisfied by reactions (3) and (4) and these reactions may proceed until the partial pressures of H and Br are exceedingly small. The condition for the possibility of (5) occurring is—

$$\log_{10} \frac{p_{\text{H}} p_{\text{HBr}}}{p_{\text{Br}} p_{\text{H}_2}} - \log_{10} K_p > 0 \quad (7)$$

where p_{H} , etc., are the partial pressures of the gases and K_p is the equilibrium constant (using partial pressure terms) at ordinary temperature. The value of the latter may be approximately evaluated by Nernst's heat theorem if the value of the heat of the reaction and the chemical constants of reactants and resultants are known. The former Warburg estimates to be + 6000 cal.; employing this figure the value of $\log_{10} K_p$ becomes - 5.4. With the experimental conditions employed, the smallest value of $p_{\text{HBr}}/p_{\text{H}_2} = 0.016$, the log of which is - 1.8; it follows therefore that reaction (5) is possible until a very small value of the ratio $p_{\text{H}}/p_{\text{Br}}$ is reached. In an analogous way, it may be shown that reaction (6) cannot occur under the conditions of the experiment. Also, since the velocity of reaction (3) is proportional to the square of the very small concentration of atomic hydrogen, while that of (5) is proportional to the product of the concentrations of atomic hydrogen and HBr, reaction (3) may be neglected in comparison with (5). We thus arrive at the conclusion, that after the primary process (2), the secondary reactions (4) and (5) take place, the sum of the whole being represented by



One quantum, therefore, causes a decomposition of two molecules, one molecule being decomposed directly, the other by a secondary process involving a resultant of the primary process. The assumption having been made that the primary effect of the light is to decompose HBr into its component atoms, the question naturally arises:—Is the energy supplied sufficiently great to effect this?

The amount of energy required to convert one gram-molecule of HBr into atomic hydrogen and bromine may be calculated, if we know the heats of dissociation of hydrogen and bromine and if we assume at

the same time that in these cases, in which nascent atoms are produced, that the heats of dissociation are identical with the energies of activation. Taking with Warburg the heat of dissociation of hydrogen to be 95,000 cal. per gram-molecule and that of bromine as 58,800 cal., we obtain as the required value 89,500 cal. The value of $1/p$, *i.e.* the number of cal. absorbed by one gram-molecule of a photolyte (*cf.* Table I.) for light of wave-length 0.209μ is 135,900 cal., and for that of 0.253μ , 112,300 cal. and therefore the energy supplied at both wave-lengths is sufficiently great.

For the second reaction recorded in Table II., the photolysis of hydriodic acid, it was found possible to carry out experiments with light of three wave-lengths, namely 0.207μ , 0.253μ , and 0.282μ , and the reaction serves as a still better test of Einstein's law. The method of experimentation employed by Warburg (*Sitzungsber. Preuss. Akad.*, 1918, p. 300) was much the same as in the previous case. The gas employed was a mixture of HI and H_2 , the partial pressures of the former varying between 80 and 300 mm. mercury. Table IV. gives the results obtained using light of wave-length 0.207μ and shows the accuracy attainable in such measurements.

TABLE IV.

PHOTOCHEMICAL DECOMPOSITION OF HI (WARBURG).

p_{HI} .	Wave-length 0.207μ .		
	A .	$E \times 10^6$	$\phi \cdot 10^6$.
82.4	0.980	318	1.44
88.3	0.997	342	1.44
112.7	0.993	362	1.35
112.7	0.990	327	1.54
83.9	0.983	297	1.37
80.2	0.967	360	1.43
86.9	0.984	313	1.48
			Mean = <u>1.44</u>

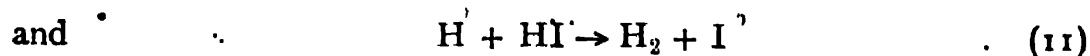
The first column gives the partial pressure of the hydriodic acid in the gas mixture, and the second the fraction of the incident light energy absorbed by the gas. E denotes the energy in cal. absorbed per second and ϕ the number of gram-molecules of HI decomposed per calorie absorbed. The values of $\phi \times 10^6$ at the three wave-lengths 0.207μ , 0.253μ , and 0.282μ were found to be 1.44, 1.85, and 2.08 respectively.

The mechanism of this reaction is exactly analogous to that of the photochemical decomposition of HBr. After the primary reaction



there follow—





the process—



being excluded on similar grounds to those already employed for (6).

As with HBr therefore one quantum decomposes two HI molecules and $\phi = 2p = 2\lambda/28,443$. The agreement between theory and experiment is within the experimental error. The energy necessary to decompose one gram-molecule of HI into atomic hydrogen and iodine is less than the corresponding quantity for HBr, being approximately 65,000 cal.

The Photochemical Formation and Decomposition of Ozone.

If oxygen be subjected to ultra-violet light of high frequency ozone formation ensues. Warburg (*Sitzungsber. Preuss. Akad.*, 1912, p. 216; *ibid.*, 1914, p. 872) studied the process using oxygen at high pressures (up to 300 atmospheres) in order to render possible measurements with light of wave-length as long as 0.253μ which is absorbed by oxygen at sufficiently high concentrations but not measurably at atmospheric pressure. The ozone formed was measured by absorption in potassium iodide solution and titration of the liberated iodine. If we assume that the primary process in this case may be represented by—



i.e. dissociation of oxygen into atomic oxygen, then the secondary processes (14) and (15) appear possible—



If further we assume that (15) does not occur to a measurable extent, the net effect will be the sum of (13) and twice (14), that is, one quantum would cause the decomposition of *three* oxygen molecules forming two of ozone. The results obtained are shown in Table V.

TABLE V.

Apparatus.	Pressure kg./cm ²	ϕ . 10 ⁵ .		
			0.209 μ .	0.253 μ .
ii.	125	2.09	1.47	1.55
	125	1.94	1.48	
ii.	300	1.74	0.78	0.83
Theoretical value (3 p) = 2.19			3p = 2.67	

This shows that the assumptions made by Warburg hold approximately for the reaction effected by light of 0.209μ at the lower pressure, but at the higher pressure the photochemical efficiency decreases. With light of 0.253μ the amount of oxygen converted into ozone is decidedly less than that predicted and also the effect of pressure in reducing the value of ϕ is greater. This behaviour cannot be accounted for by the fact a certain fraction of the ozone formed is decomposed again by light of this wave-length; correcting for this gives the values in the last column which are only a few per cent. higher than the ones experimentally obtained.

The reverse process, the photochemical decomposition of ozone seems to be an extraordinarily complicated one. Considering again the results of Warburg (*Sitzungsber. Preuss. Akad.*, 1913, p. 644), only one wave-length was here employed, *viz.* 0.253μ , approximately the maximum of the strong ozone absorption band in the ultra-violet. Experiments were carried out employing mixtures of ozone with oxygen, with nitrogen, and with helium. For ozone-oxygen mixtures it was found that the value of ϕ varies markedly with the concentration of the ozone; it decreases with decreasing ozone content until a concentration of 0.5 vol. per cent. is attained after which a further decrease in concentration does not alter the value of ϕ . With mixtures of ozone and nitrogen an analogous behaviour is followed, yet the limiting value of ϕ for small ozone concentrations is 3.8 times as large, *i.e.*, 0.95×10^{-5} instead of 0.25×10^{-5} . Considering alone these limiting values the behaviour of nitrogen in increasing the extent of ozone decomposition is accounted for in the following manner. If we assume with Warburg that the primary process is—



then the secondary processes—



become possible. Of these three reactions (17) does not influence the ozone concentration, (18) increases it, (19) diminishes it. According to Einstein's law, the primarily decomposed ozone, *i.e.* that decomposed according to (16) will be p gram-molecules / cals. Then if all the oxygen atoms formed reacted according to (17), the *secondarily* decomposed ozone would be nil, if according to (18) — p , and if according to (19) + p . It follows, therefore, that in mixtures of ozone and oxygen the total number of gram-molecules of ozone decomposed *per calorie* absorbed must lie between zero and $2p$, depending on the relative extent of the secondary processes. For mixtures of ozone and nitrogen there is the possibility of either ozone or oxygen atoms reacting with nitrogen. As, however, no oxides of nitrogen can be detected by chemical means after illuminating the gas mixture, it may be concluded that nitrogen acts in this reaction as a chemically indifferent gas. Since in these

mixtures the only oxygen present is that formed by reactions (16), (17) and (19), reaction (18) will take place to a much less degree than in ozone-oxygen mixtures, and therefore the value of ϕ will be greater. If, as is permissible, we exclude (18) entirely for ozone-nitrogen mixtures, the value of ϕ should lie between ρ and 2ρ . This conclusion is confirmed experimentally as the value found for ϕ is 0.95×10^{-5} whilst that of ρ for 0.253μ is 0.89×10^{-5} . An unexpected result however was obtained on employing helium as a diluent to the ozone. Instead of finding in such a mixture weak in ozone the same value for ϕ as that in the presence of nitrogen, the higher value 1.52×10^{-5} was obtained. Since both helium and nitrogen presumably act as chemically indifferent gases in this reaction, it is difficult at present to suggest a reason for this difference. Whatever may be the explanation, it is interesting to note that the value $\phi = 1.52 \times 10^{-5}$ is nearly equal to the value 2ρ , the theoretical value assuming (16) as the primary process and (19) as the only secondary. In the most concentrated ozone mixtures studied, either in oxygen or nitrogen the value found for ϕ becomes greater than that of 2ρ . This is probably connected with the fact that the process: $2O_3 \rightarrow 3O_2$ is exothermic and the energy evolved in one of its component secondary processes may be transferred by molecular collision, some ozone molecules being in this way activated. In dilute ozone mixtures the effect would not be marked owing to the greater probability of the activating molecule carrying the excess energy¹ of losing this before colliding with an ozone molecule.

Another anomaly of the photochemical decomposition of ozone was pointed out by von Bahr (*Ann. Physik* [iv], **33**, 598, 1910) who observed that when the total pressure of a mixture of ozone and oxygen was lowered below 200 mm. mercury the rate of photochemical de-ozonisation increases in a marked manner, which means that the values of ϕ at small total pressures would be much greater than those given above.

The Photochemical Decomposition of Ammonia

Little need be said about this reaction. The extent of decomposition was measured (Warburg, *Sitzungsber. Preuss. Akad.*, 1911, p. 746) following the pressure changes registered on a differential manometer containing mercury, the pressure of ammonia was 800 to 900 mm., and only one wave-length employed, *viz.* 0.207μ . The mean value of $\phi \times 10^5$ obtained was 0.17 which is less than a quarter of the corresponding value of ρ .

Deviations from Einstein's Law. Theoretical Considerations.

Before discussing the remaining reactions of Tables II. and III. it will be convenient at this stage to deal with certain theoretical considerations arising out of the reactions of the preceding paragraphs. We have seen that by making legitimate assumptions regarding the

¹ Warburg suggests that this is the oxygen formed by (17).

secondary processes, the results obtained in the cases of the photolysis of hydrogen iodide and hydrogen bromide may be quantitatively accounted for on the basis of Einstein's law; these examples also make clear the importance of distinguishing between the primary process and the total observed extent of the reaction. One of the best criteria of the validity of Einstein's law is that ϕ should increase with increasing wave-length of the light employed. Although this is so in the examples just cited, in most cases the reverse is true, *i.e.* the photochemical efficiency of the light decreases as its wave-length is increased. The discrepancy has been considered by Weigert (*Zeitsch. Elektrochem.*, **23**, 357, 1917) and by Warburg (*ibid.*, **26**, 54, 1920) whose conclusions are similar. According to these investigators the deviations are essentially due to loss of energy on the part of the activated molecule as a result of collision, this energy appearing as heat. The absorption processes for an isolated molecule and for a molecule surrounded by others will in general be different. In the infinitely dilute state the absorption bands of atoms and molecules appear as lines, but as the concentration of material is increased, the lines broaden into bands, the widths of which continually increase with increasing concentration. For an isolated molecule the radiant energy absorbed must be quantitatively changed into internal atomic energy, but this does not apply if the electron orbits of the absorbing molecule are affected by the presence of neighbouring molecules. In the latter case, during the act of absorption there will be an energy interchange between the absorbing molecule and its neighbours, and thus part of the absorbed energy is expended on the neighbouring molecule. The magnitude of this energy interchange is different for different absorbing molecules since it depends on the relative velocities and proximities of the molecules during the act of absorption. It is therefore possible for some absorbing molecules to transfer so much energy to their neighbours that the amount remaining is insufficient to cause them to decompose or to enable the primary process to occur. Also it is clear that the loss of energy by the absorbing molecule will increase with increasing pressure in the case of gaseous systems and that the effect should be more marked in the liquid state where the density is greater.

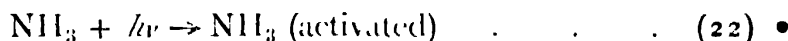
Further, the greater the frequency of the light employed, the less marked should this effect be, because of the fact that owing to the larger quantum absorbed the greater the probability becomes that the quantity of energy remaining in the absorbing molecule is sufficiently large to decompose it. The decrease in ϕ experimentally found in many reactions with increasing wave-length is in this manner qualitatively accounted for.

Another condition which must be fulfilled if Einstein's law is to hold was also postulated by Warburg (*loc. cit.*). It follows, if we make the assumption for a given photochemical process, that the primary effect of the light is a decomposition, *e.g.* $AB + h\nu \rightarrow A + B$, that the process can only occur if the absorbed energy quantum is greater than the energy required to decompose the molecule. If we

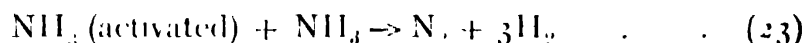
denote by q cal. the energy necessary to decompose one gram-molecule of the absorbing substance, photochemical action should only ensue when the light employed is such that $1/p > q$. Although in many cases the value of q is only approximately known it may be definitely stated, however, that photochemical action does occur even when $1/p < q$. Such is the case for the photochemical decomposition of ammonia by light of wave-length 0.207μ . The primary process here cannot be represented by—



since the value of q for the process (21) is at least 200,000 cal., while the value of $1/p$ for light of this wave-length is only 137,300 cal. (Table I). It must therefore be assumed that the primary reaction is not a decomposition of the ammonia molecule but an activation, i.e. the formation of a molecule with a higher energy content than the normal—

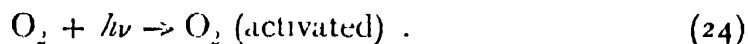


Further, when this activated molecule collides with a non-activated ammonia molecule, decomposition may occur according to equation (23)—

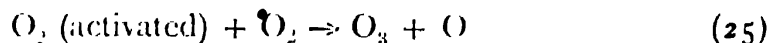


The amount of energy necessary for the activation in reaction (23), according to Warburg, is only 22,000 cal. per gram-molecule activated, or per two gram-molecules of ammonia decomposed.¹ If all the absorbing molecules reacted in this way, we should therefore expect to find $\phi = 2p = 1.47 \times 10^{-5}$, while the value obtained is only 0.17×10^{-5} . It would therefore appear that all the collisions experienced by an activated molecule are not of the type necessary to initiate the reaction.

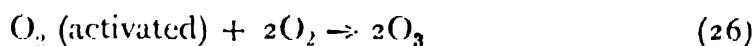
Another reaction which probably occurs without primary decomposition of the absorbing molecule is the photochemical formation of ozone from oxygen. The value of q , the heat of dissociation of oxygen is not accurately known, but may be taken with Lewis (*Trans. Faraday Soc.*, **17**, Part II, 1921) as about 150,000 cal. The value of $1/p$ for light of wave-length 0.253μ is only 112,000 cal., yet ozone is formed using light of this wave-length from oxygen under high pressure. The mechanism of ozone formation may now be—



followed either by



or



¹The value 22,000 cal. is almost certainly too small, however, since it is obtained by equating the energy of activation to the heat of reaction. This is probably permissible when the reaction considered involves the formation of nascent atoms, as in the photochemical decomposition of HBr, but is not necessarily so in such cases as the one under consideration.

In (25) the first oxygen molecule possibly requires an activation of 109,000 cal., in (26), of 68,000 cal.¹ With light of wave-length 0.207μ the value of $1/p$ is 137,000 cal.; this amount may be sufficiently large to decompose oxygen into its atoms, as it is possible that the value 150,000 cal. may be too high. In either case, as would be anticipated, the value found for ϕ is nearer the theoretical than that employing the longer wave-length. The influence of pressure in diminishing the yield in this reaction is explained by the considerations already referred to above.

These two reactions, the formation of ozone and the decomposition of ammonia illustrate the fact that photochemical action does not suddenly cease when the wave-length of the light employed is increased to a value such that $1/p < q$, but that photolysis still occurs, though with diminishing yields.

Photochemical Reactions involving Chlorine or Bromine.

The deviations from Einstein's law which we have so far encountered have been those in which the number of molecules reacting is less than anticipated, and two effects that might account for this have been given in the preceding paragraph. We have now to consider a reaction for which the reverse is true—the well-known photochemical union of hydrogen and chlorine—in the light of the theory advanced by Nernst (*Zeitsch. Elektrochem.*, **24**, 335, 1918).² According to the calculations of Bodenstein (*loc. cit.*), and Gohring (*Zeitsch. Elektrochem.*, **27**, 511, 1921) based on the experiments of Bodenstein and Dux (*Zeitsch. physikal. Chem.*, **85**, 297, 1913) it appears that, for each quantum absorbed,³ about half a million molecules of hydrochloric acid are formed.

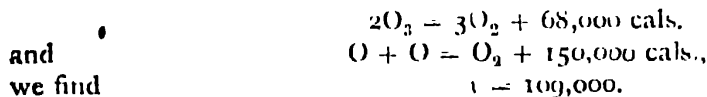
Nernst explains this enormous sensitivity to light as being due to a series of secondary spontaneous thermal reactions forming a cycle.

¹ The value 109,000 cal. for the energy of activation of the first oxygen molecule in (25) is obtained as follows.—

Let x cal. be the heat absorbed in the reaction—



Combining this equation with the thermochemical equations—



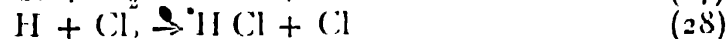
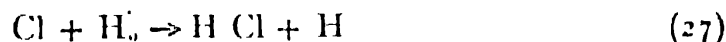
This will represent therefore the energy of activation of an oxygen molecule necessary to enable (25) to proceed, provided that we assume that the reverse reaction requires no energy of activation. This is possibly true owing to the reverse reaction involving a nascent oxygen atom.

The value 68,000 cal. for the energy of activation of the oxygen molecule in (26) is a minimum one obtained by equating the energy of activation to the heat of reaction, *cf.* preceding footnote.

² For an alternative explanation of the excessive photochemical yield, *cf.* Baly and Barker, *J. C. S.*, **119**, 653, 1921.

³ By the chlorine.

As a result of absorption of light (wave-length *circa* 0.330μ), chlorine is dissociated into free chlorine atoms. By application of the Heat Theorem, Nernst shows that the processes—



are both attended by a diminution of free energy and may, therefore, take place. Assuming that they actually occur, it will be seen that a cycle ensues, the chlorine atoms produced by (28) again reacting with H_2 according to (27), and the two reactions continue to take place, so that a very small number of free chlorine atoms can produce a relatively large amount of hydrochloric acid. Naturally a limit is set to this amount since eventually the chlorine atoms and hydrogen atoms will combine to form Cl_2 , H_2 and HCl . This mechanism also explains the large inhibiting effect of certain impurities, notably oxygen, their action being to combine with and thus cause a decreased concentration of the hydrogen and chlorine atoms. Thus if oxygen be the inhibitor, it forms ClO_2 with the chlorine atom, and is then regenerated by reaction of the ClO_2 with atomic chlorine; thus a small concentration of oxygen has the effect of greatly diminishing the photochemical yield of hydrochloric acid, yet its concentration remains constant. In further support of the theory, Nernst shows that an analogous cycle for a mixture of hydrogen and bromine is not possible, since the reaction—

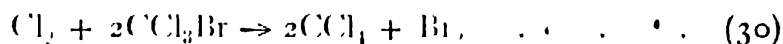


cannot take place to an appreciable extent. In agreement, it was shown by Pusch (*Zeitsch. Elektrochem.*, **24**, 336, 1918) that hardly any HBr is formed when the mixture is strongly illuminated at ordinary temperatures.

We have, therefore, in the photochemical formation of hydrochloric acid and the action of light on mixtures of hydrogen and bromine two examples of processes for which Einstein's law (as usually stated) is far from being obeyed, the reason in each case being that the secondary reaction actually measured is not equivalent in amount to the primary process, or, in the terminology usually employed, hydrogen is not a suitable acceptor.¹ That suitable acceptors exist for chlorine and bromine photochemically activated, Nernst, Pusch, and Noddack proceeded to show. Thus, a suitable acceptor for bromine was found in hexahydrobenzene, after the trial of other hydrocarbons, such as hexane and heptane, which react to a greater extent than predicted by Einstein's law. The results obtained with gaseous mixtures of hexahydrobenzene and bromine, however, were found, after correcting for a slight "dark" reaction, to be in agreement with the calculated within the experimental error, *i.e.* for each quantum absorbed one molecule of bromine disappears. (See Table III, Pusch (*loc. cit.*) and Noddack, *Zeitsch. Elektrochem.*, **27**, 359, 1921.)

¹ This term is used to denote the substance which reacts with the product formed as a result of the primary "light" process.

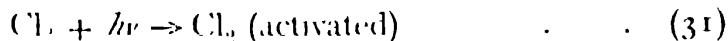
The acceptor for chlorine has to conform to certain conditions. It has to be sufficiently stable not to be chlorinated in the dark, it must contain no hydrogen otherwise there is a possibility of disturbing secondary reactions, it must be either a gas or a liquid in which chlorine is soluble, etc. The substance finally chosen by Noddack (*loc. cit.*) was trichlorobrommethane, a colourless liquid which dissolves chlorine readily. If the solution thus formed be exposed to violet light, the net result of the change is expressed by—



The reaction was studied using light of two wave-lengths 0.410μ and 0.449μ , and the bromine formed determined by spectrophotometric measurements. The results obtained (Table III.) show that for each quantum absorbed, one chlorine molecule disappears with the formation of one of bromine.

Noddack also observed that if the reaction were allowed to proceed in carbon tetrachloride as a solvent,¹ the yield of bromine was diminished, but this was later shown by Gruss (*Zeitsch. Elektrochem.*, **29**, 144, 1923) to be due to traces of impurity in the carbon tetrachloride. The latter found that if the solvent be sufficiently purified, the velocity of the photochemical reaction is independent of the relative concentrations of CCl_3Br and CCl_4 , at least until the ratio $\frac{\text{moles of CCl}_4}{\text{moles of CCl}_3\text{Br}}$ exceeds 80.

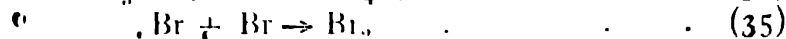
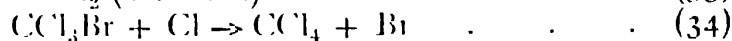
Employing silicon tetrachloride as a solvent, a similar result was obtained. The mechanism of the process may be formulated in two different ways; which of these is the more probable cannot at present be stated. The primary process in general is best regarded not as a decomposition of the molecule as we have assumed in the cases of HI , HBr and O_3 , but simply as the absorption of an energy quantum by a molecule and its consequent conversion into one of higher energy content, most probably by the passage of one or more electrons from inner to outer orbits. In the case under discussion we may write for the primary process—



The activated chlorine molecules may now either (a) react directly with trichlorobrommethane molecules, *i.e.* we have the trimolecular “dark” reaction—



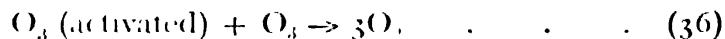
or (b) they may decompose thermally into chlorine atoms which then react—



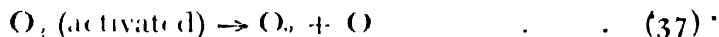
Of course, the reaction may take place by (a) and (b) simultaneously.

¹ CCl_4 does not absorb any of the light.

The reaction of Table I. so far unconsidered is the decomposition of ozone in the presence of either chlorine or bromine. Weigert (*Zeitsch. Elektrochem.*, **14**, 591, 1908) showed that if a mixture of chlorine and ozone be subjected to the action of violet light, which is absorbed by chlorine but practically not at all by ozone, the latter decomposes. This is an example of a sensitised photochemical reaction, the concentration of the absorbing substance—chlorine—remaining unchanged. Einstein's law, as usually formulated, cannot therefore apply. Bonhoffer (*Zeitsch. für Physik*, **13**, 94, 1923) showed, however, that there is a simple relation between the number of quanta absorbed by the chlorine and the number of ozone molecules decomposed. The ratio found is two molecules per quantum; in addition, the reaction velocity is independent of the concentration of ozone. The results may be interpreted to mean that the quantum absorbed by a chlorine molecule is transferred to an ozone molecule by collision, and that there then follows either the reaction—

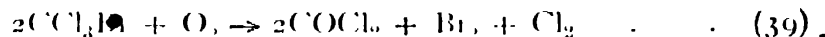


or the reactions—



- In the presence of bromine as sensitiser, Bonhoffer found that not two but thirty molecules of ozone are decomposed per quantum absorbed. It is difficult to supply a satisfactory theory to account for this difference. The results apparently show that the mechanism of sensitisation is not so simple as outlined above, but that the nature of the sensitiser must be considered, possibly from the point of view of the capacity of its activated form to react with ozone to form unstable complexes.

The activity of a given sensitiser depends on the reaction which is sensitised. Thus bromine, which has a large effect on the decomposition of ozone, acts normally as a sensitiser in the reaction—

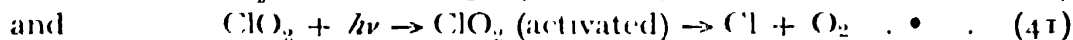
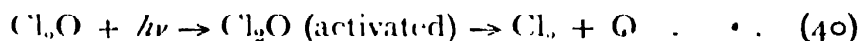


occurring in CCl_4 solution. Gruss (*loc. cit.*) found that the velocity of this reaction was independent of the concentration of O_2 and CCl_3Br , and that for each quantum absorbed by the bromine two molecules of CCl_3Br reacted according to (39)

Reactions in Liquid Media.

In general these present more complications than do gaseous reactions. We have already discussed one example, the chlorination of trichlorobromomethane; here the reaction follows the predicted course either in presence or absence of CCl_4 as solvent. The only other examples of simple behaviour are those obtained by Bowen (*Trans. Chem. Soc.*, **123**, 1799, 1923), namely, the photochemical decomposition of the oxides of chlorine, Cl_2O and ClO_2 dissolved in CCl_4 . It was

found that the decomposition is 80 to 90 per cent. of the theoretical and ϕ is independent of the concentration of the chlorine oxide in both cases. The photochemical decomposition of NCl_3 in the same solvent was also investigated. In this case the results indicated that more than one molecule decomposes per quantum absorbed. The light employed (wave-length 0.445μ) corresponds to an activation of 65,000 cal. per gram-molecule and Bowen calculates that this energy is sufficiently large to enable the reactions—



to take place.

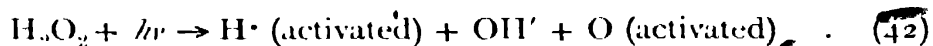
The other reactions of Table III. were all effected in aqueous solution and all exhibit the feature that the value of ϕ depends on the concentration of the photolyte. Taking first the photochemical decomposition of H_2O_2 , apparently the simplest chemically, this is an exothermic reaction the velocity of which is proportional to the amount of light absorbed, *i.e.* the reaction follows a unimolecular course. It has been quantitatively studied by Henri and Wurmser (*Comptes Rend.*, **156**, 1012, 1913) who found that the extent of decomposition is much greater than that given by Einstein's law,¹ and by Kornfeld (*Zeitsch. wiss. Phot.*, **21**, 66, 1921) whose results may be summarised thus:—

1. The photochemical decomposition of H_2O_2 in aqueous solution is markedly sensitive to impurities and to the concentration of H^+ and OH' . Increase of H^+ decreases the velocity, small additions of OH' increase it slightly while larger amounts cause a marked fall.

2. Using monochromatic light of wave-length 0.310μ , the number of molecules of H_2O_2 decomposed per quantum absorbed depends on the concentration of H_2O_2 , falling from 77 with 0.05 normal H_2O_2 to 24 with 0.016 normal.

3. Addition of acid lowers these quantities and diminishes somewhat their variability with the concentration of H_2O_2 .

These results clearly indicate the large effect produced by secondary reactions; as in the hydrogen-chlorine reaction a large and variable excess yield is obtained. (Note that both reactions are exothermic.) Kornfeld develops an interesting theory to account for the great velocity of decomposition, its dependence on the concentration of H^+ and OH' , and the fact that over a wide range the reaction is apparently of the first order. The mechanism proposed is complicated; it assumes that the primary process is—



after which numerous secondary processes are possible. Henri and Wurmser showed that in contradiction to the requirements of Einstein's

¹ Henri and Wurmser found that as many as 80 molecules of H_2O_2 could be decomposed by one quantum. The results given in Table III. refer to conditions such that the decomposition is much less.

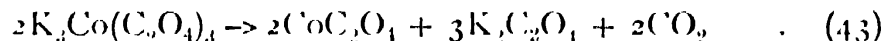
law ϕ does not increase with increasing λ and Kornfeld's theory also accounts for this.

Boll (*Comptes Rend.*, **157**, 115, 1913; *Ann. Chim. Phys.* [ix], **2**, 1, 1914) determined the rate of photolysis of the chloroplatinic acids in aqueous solution which results in their reduction. These endothermic reactions are apparently bimolecular: the value of ϕ increases with increasing concentration of photolyte at constant wave-length, and diminishes with increasing wave-length at constant concentration. This variation is shown in Table VI. in which the results obtained with the tetra-acid $\text{PtCl}_4(\text{OH})_2\text{H}_2$ are given:—

TABLE VI.
PHOTOLYSIS OF $\text{PtCl}_4(\text{OH})_2\text{H}_2$.

Concentration			1 N.	
	$\phi \times 1$			$\phi \times 10^5$
0.2	0.34	0.546	0.0072	1.91
0.5	0.831	0.310	0.101	1.68
2.0	3.15	0.251	1.66	0.89
		0.238	3.52	0.83

The velocity of the photochemical decomposition of potassium cobaltioxalate in aqueous solution was measured by Vranek (*Zeitsch. Elektrochem.*, **23**, 336, 1917). The reaction proceeds according to the equation—



The cobaltioxalate possesses two absorption bands, one with a maximum at $\lambda = 0.426$, the other at $\lambda = 0.605$; only wave-lengths within the former band are effective in decomposing it. The apparent order of the reaction is between one and two and Vranek states that the value of ϕ is independent of the concentration, but this is doubtful in view of what is found for all the other processes in aqueous solution so far investigated. The results given in Table III. show that ϕ increases approximately linearly with *decreasing* wave-length.

Both this reaction and that investigated by Boll are evidently of a somewhat complex nature and in neither does ϕ increase as λ is increased. In fact, the exact opposite is true. This is possibly accounted for by the theory given earlier, *i.e.* loss of activation by non-reactive collision. The probability seems to be that in aqueous solution the more concentrated the solution the less is the energy lost by such non-reactive collisions.

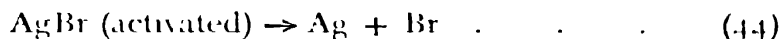
Since both the photolytes are relatively complex substances, Warburg (*Sitzungsber. preuss. Akad.*, 1918, p. 1228) studied a simpler reaction, the photochemical conversion of potassium nitrate into potassium nitrite

and oxygen. Even with this substance, however, complications persist, since the reaction velocity is sensitive to additions of acid and alkali and in order to obtain comparable results, it was found necessary to work with solutions made N/3000 with respect to alkali. The nitrates of Li, Na, K, Mg, Ca, Sr, Ba give the same results provided solutions of the same equivalent concentration are used, but HNO_3 is much less sensitive to light. In Table III. will be found the results obtained with N/3 solutions of KNO_3 at different wave-lengths. The effect of varying the concentration at constant wave-length is in the usual direction, though the variation is not so marked as in the case of $\text{PtCl}_4(\text{OH})_2\text{H}_2\text{O}$. The energy necessary to decompose the NO_3 group (in aqueous solution) into $\text{NO}_2 + \text{O}$ is estimated by Warburg to be 101,000 cal. per gram equivalent, so that the energy supplied at 0.287μ and 0.253μ (but not at 0.282μ) is sufficiently large. The values of ϕ , however, are only about one-quarter of the theoretical.

The reciprocal transformation of maleic and fumaric acids in aqueous solution was also investigated by Warburg (*Sitzungsber. Preuss. Akad.*, 1919, p. 960). The stable acid is fumaric acid, if a solution of either of these acids is subjected to ultra-violet light, a stationary state will eventually be reached when the ratio of maleic acid to fumaric acid is approximately 7 : 3. The velocity of both processes was measured, and the results (Table III.) indicate a very small photochemical efficiency. This may be due, according to Warburg, to the primary process being a driving apart of two portions of the absorbing molecule, which may then reunite to form the original molecule or its isomer, the extent to which the latter takes place being small. The influence of alteration of the concentration is not great, yet curiously ϕ increases with increasing concentration for the reaction fumaric $\rightarrow$ maleic, but decreases for the reverse change.

Photochemical Reactions in the Solid State.

It has been demonstrated by Noddack and Eggert (*Sitzungsber. Preuss. Akad.*, 1921, p. 631; *ibid.*, 1923, p. 116) that Einstein's law is applicable to the action of light on silver bromide in a photographic dry-plate. The reaction which occurs may be represented by—



The silver atoms liberated are equal to the number of quanta absorbed, provided that a suitable acceptor, in this case the gelatine, reacts with the liberated bromine. Three wave-lengths were employed, 0.436μ , 0.405μ , and 0.365μ , and correction was made for the light scattered and that absorbed by the gelatine. Equivalence between silver atoms formed and quanta absorbed is only found for the first period of illumination; later, as also when intense illumination is employed, the yield of silver is too small, evidently owing to recombination of silver and bromine which occurs when the gelatine in the neighbourhood of the AgBr particles is fully brominated. Weigert (*Sitzungsber. Preuss. Akad.*; 1921, p. 641) has also

shown that Einstein's law applied to the action of light on a silver chloride emulsion yields correct results if applied to the initial stages of the reaction, though his experimental data are not in good agreement on some points with those of Eggert and Noddack.

Summary.¹

This survey of photochemical reactions shows that the ratio molecules decomposed / quanta absorbed may vary over wide limits though in a large number of cases its value is not far removed from unity. The simple quantitative relations found in such reactions as the photochemical decomposition of hydrobromic and hydriodic acids and the photochemical chlorination of trichlorobromomethane form strong evidence for the view that the ratio $\frac{\text{energy absorbed}}{h\nu}$ is equal to the number of absorbing molecules in all cases. Apparently, however, this is the only *general* conclusion which may be inferred from the measurements above described. The processes which occur between the act of absorption and the production of the final products are those which determine the value of the ratio molecules of photolyte decomposed / quanta absorbed. Depending on the nature of the reaction, the wave-length of the light employed and other factors, these processes may be such as to cause a large difference between the number of absorbing molecules and of those decomposed. Only in a few reactions, and in those only within certain narrow spectral limits, has the ratio been found to be unity.

¹ See a paper by Nernst and Noddack, *Sitzungsber. Preuss. Akad.*, 1923, p. 110.

APPENDIX VIII.

THE DIMENSIONS OF THE CHEMICAL CONSTANT.

(Cf. F. A. Lindemann, *Phil. Mag.*, **39**, 21 (1920)).

THE general equation for the vapour pressure of a solid derived by integrating the Clapeyron equation is of the form—

$$\log p = \int \frac{\lambda}{RT^2} dT + C = \int \frac{\lambda_0 + \int_0^T C_f d'T + \int_0^T C_p d'T}{RT^2} dT + C \quad (1)$$

where λ is the latent of vaporisation, λ_0 the same at absolute zero, C_f and C_p the molecular heats of the solid and gas respectively at constant pressure, R is the gas constant per gram-molecule, and C the chemical constant of the substance. (Following the convention adopted in Chap. IX. in connection with the "characteristic constant" i and the allied quantity the chemical constant C , the above equation would be taken as involving logarithms to the base 10 with pressure in atmospheres. The considerations dealt with below are equally applicable to either i or C).

The question of the correct dimensions of the chemical constant is of great importance as it is intimately bound up with the question of the validity of the degradation theory of gases (cf. Chaps. IV. and IX.). The point is, whether the chemical constant has the dimensions of the logarithm of a pressure, or whether it has the dimensions of the logarithm of a pressure divided by a temperature θ to the power $5/2$, the temperature θ here referred to being a constant characteristic in some way of the substance considered.

The first view, namely, that the dimensions of C are those of the logarithm of a pressure appears to be justified at first sight by the fact that $\frac{\lambda}{RT^2} dT$ in equation (1) is dimensionless, *i.e.* a pure number, and consequently C is the logarithm of a pressure. This conclusion, as Lindemann shows (*vide infra*), really entails the assumption that the molecular heat of the gas equals that of the solid in the neighbourhood of absolute zero; that is that C_p decreases to zero in the neighbourhood of absolute zero. This, it will be recalled, is the main feature of the degradation theory of gases.

The second view, namely, that the dimensions of C are those of the logarithm of a pressure divided by a temperature to a certain power, is arrived at by assuming that the gas laws hold down to the lowest temperatures, *i.e.* that C_p retains its value $5/2$ for a monatomic gas even at the lowest temperatures. If, therefore, we could determine with precision the dimensions of C we would possess a valuable criterion for testing the degradation theory. The case considered is that of a monatomic vapour in contact with the solid form. Lindemann proceeds in the following manner:—

If C_f and C_p are analytical functions of T one may write—

$$\int_0^T C_f dT = a_0 + a_1 T + a_2 T^2 + \dots$$

and
$$\int_0^T C_p dT = b_0 + b_1 T + b_2 T^2 + \dots$$

where the coefficients are energy terms. Hence equation (1) becomes—

$$\log p = \frac{\lambda_0}{RT} - \frac{b_0 - a_0}{RT} + \frac{b_1 - a_1}{R} \log T + \frac{b_2 - a_2}{R} T + \dots \quad (2)$$

It is clear that every term of this series is a pure number with the exception of the third, which has the dimensions of the logarithm of a temperature to the power $\frac{b_1 - a_1}{R}$. One may conclude, therefore, that the dimensions of C are those of the logarithm of a pressure divided by a temperature to the power $\frac{b_1 - a_1}{R}$. It is implied in this statement that $b_1 - a_1$ is not zero.

Now b_1 and a_1 are clearly the atomic heats of the gas and of the solid respectively at the absolute zero, and there seems little doubt that a_1 is zero (Nernst's heat theorem). Therefore, if the value of $b_1 - a_1$ can be found, it will give us the value of b_1 itself, *i.e.* the value of the molecular heat of the monatomic gas at absolute zero and in the neighbourhood thereof.

The probable form of the chemical constant C may be derived by means of the following dimensional considerations. In the case of a monatomic gas, we may suppose that C depends only on the mass m of the molecule, the gas constant k per molecule, Planck's constant h , and some temperature θ characteristic of the gas in question. Let us assume for the moment that C has the dimensions of the logarithm of a pressure. Then—

$$C = \log p = \log m^x + \log k^y + \log h^z + \log \theta^u + \text{a constant.}$$

The dimensions of pressure being $\frac{M}{L^2}$, the dimensions of k being energy/temperature = $\frac{ML^2}{T^2\theta}$, the dimensions of h being those of action,

namely, energy $\propto$ time = $\frac{ML^2}{t}$; it follows that the dimensional equation is—

$$\frac{M}{L^2} = M^x \left(\frac{ML^2}{\theta^2} \right)^y \left(\frac{ML^2}{t} \right)^z \cdot \theta^u,$$

whence $x = \frac{3}{2}$, $y = \frac{5}{2}$, $z = -3$, and $u = \frac{5}{2}$,

so that, on this basis, C would take the form—

$$\log \frac{m^{3/2} k^{5/2} \theta^{5/2}}{h^3}$$

(Naturally dimensional considerations give no information regarding any pure numbers which are also almost certainly involved in the expression for C.)

If we now assume, as we have above seen reason to do, that the dimensions of C are those of the logarithm of a pressure divided by a temperature (θ) to the power $\frac{b_1}{R} + a_1$, dimensional considerations will lead to an expression for C having the following form—

$$\log \frac{m^{3/2} k^{5/2} \theta^{5/2} \left(\frac{p}{R} \right)^{\frac{b_1}{R} + a_1}}{h^3}$$

Hence C must be expressible thus—

$$C = C_0 + \frac{3}{2} \log M + (5/2 + b_1/R + a_1/R) \log \theta \quad (3)$$

where C_0 is a constant, M the atomic weight, and θ some unknown temperature which can only depend upon the temperature at which, according to the degradation theory, the gas laws cease to hold.

Now it has been shown—the experimental data are given in Chap. IX, section on the “characteristic constant”—that within the limits of error the chemical constant can be written—

$$C = C_0 + \frac{3}{2} \log M \quad (4)$$

This must be in agreement with equation (3). In order that this may be so, it is evident that the term containing θ , namely $(5/2 + b_1/R + a_1/R) \log \theta$ in equation (3) must vanish. Since a_1 is zero, it is necessary that the term $(5/2 + b_1/R) \log \theta$ shall vanish. This will happen on *either* of two assumptions, *viz.* :—

(1) If C_p retains its value, $\frac{5R}{2}$, down to absolute zero, b_1/R will then be $5/2$ and the quantity inside the bracket vanishes. θ can at the same time vary with the chemical nature of the gas.

(2) If C_p falls to zero, as the degradation theory requires, then $b_1 = 0$; and the quantity inside the bracket becomes $5/2$. In this case it is necessary, in order that the θ term shall vanish, that θ itself shall be unity for all monatomic gases. This is implied, therefore, in the degradation theory of gases.

Let us consider these two possibilities a little further. If assumption (2) is correct, that is, if $b_1 = 0$, then the term $\frac{b_1}{R} - \frac{a_1}{T} \log T$ in equation (2) vanishes, and consequently all the terms in this equation are now dimensionless. Hence in this case C has the dimensions of the logarithm of a pressure.

If assumption (1) is correct, that is, if $b = \frac{5}{2}R$, it follows that C has the dimensions of the logarithm of a pressure divided by a temperature (characteristic of the substance) raised to the power $5/2$.

Of the two assumptions considered Lindemann concludes that assumption (2) is the less probable since it requires that θ shall not only be the same for all monatomic gases—even where these possess such apparently divergent characteristics as say mercury and argon possess—but that, further, this constant must possess the arbitrary value unity. If Lindemann's contention be just, assumption (2) falls to the ground and with it the degradation theory of gases. We are then left with the first assumption, namely that the molecular heat of a monatomic gas retains its constant value $\frac{5}{2}R$ down to absolute zero.

Assuming that the molecular heat thus retains its value $\frac{5}{2}R$, Lindemann shows that the chemical constant may take on a new physical significance. The procedure is as follows:

The equation for the vapour pressure may be written—

$$p = p_0 e^{\int_{\lambda_0}^T f(T) dT - \int_0^T \frac{C_p}{RT^2} dT}$$

(It is evident that $i = \log p_0$.)

The symbol $f(T)$ stands for $\int_0^T C_p dT$. Since C_p is taken to be $\frac{5}{2}R$ down to absolute zero it follows that—

$$\int_0^T \int_0^T \frac{C_p dT}{RT^2} dT = \log T^{5/2}$$

$$\text{Hence } p = p_0 T^{5/2} e^{\int_{\lambda_0}^T \frac{\lambda_0 - f(T)}{RT^2} dT}.$$

$$\text{Setting } p_0 = \frac{(2\pi)^{3/2} m^{3/2} h^{5/2}}{h^3},$$

the equation becomes

Now Stefan's constant σ , the constant of total (black body) radiation, is given by—

$$\sigma = \frac{2\pi^5}{15} \cdot \frac{k^4}{c^2 h^3}$$

Whence

$$p_0 = \frac{(2\pi)^{5/2} \cdot m^{3/2} \cdot k^{5/2}}{2 \cdot \pi^2 \cdot k^4} = 15\sigma T^4.$$

Also for a monatomic gas $m\bar{v}^2 = 3kT$, where $\bar{v}$ is the molecular velocity. Hence

$$p = \frac{45}{\pi^4} \sqrt{6\pi} \cdot \frac{c^3}{v^3} \cdot \sigma T^4 \cdot c \int_0^1 \frac{\lambda_0 - f(\lambda)}{\lambda^4} d\lambda.$$

Now $\frac{4\sigma T^4}{3c} = P$ = the radiation pressure of complete radiation of temperature T on the walls of a containing vessel. Hence—

$$p = \frac{135}{4\pi^4} \sqrt{6\pi} \cdot \frac{c^3}{v^3} \cdot P \cdot c \int_0^1 \frac{\lambda_0 - f(\lambda)}{\lambda^4} d\lambda.$$

The velocity V of sound in the gas considered is given by

$$v \sqrt{\gamma} = \frac{v}{3} \sqrt{5}, \quad \left(\text{since } \gamma = \frac{C_p}{C_v} = \frac{5}{3} \right).$$

Introducing V into the above equation we obtain —

$$p = \frac{25}{4\pi^4} \sqrt{30\pi} \cdot \frac{c^3}{V^3} \cdot P \cdot c \int_0^1 \frac{\lambda_0 - f(\lambda)}{\lambda^4} d\lambda$$

which for low temperatures, *i.e.* $f(T)$ small, becomes

$$p = 0.623 \cdot \frac{c^3}{V^3} \cdot P e^{-\frac{\lambda_0}{RT}}.$$

If any frequency, ν , is considered, the wave-length of the elastic (compressional) wave in the gas is V/ν , the corresponding electromagnetic wave having the wave-length c/ν . Now the kinetic energy of the gas molecules per c.c. is $\frac{3}{2}p$, where p is the gas pressure. Hence the energy of the gas in a cube whose side is one (compressional) wave-length is $\frac{3}{2}p \cdot \frac{V^3}{\nu^3}$. Also, the radiation density of complete radiation is given by $3P$, where P is the radiation pressure. Hence the amount of radiational energy in a cube the side of which is one electromagnetic wave-length is given by $3P \cdot \frac{c^3}{\nu^3}$.

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The ratio of these two quantities is given by the above equation as—

$$\frac{3}{2} \frac{V^3}{\nu^3} \Big|_{3P} \frac{c^3}{\nu^3} = \frac{0.625}{2} e^{-\lambda_0/RT}.$$

That is, the energy, residing in the gas in a cube whose side is one wave-length, divided by the corresponding energy in the radiation, is $0.312 e^{-\lambda_0/RT}$, i.e. 0.312 times the fraction of molecules whose energy is greater than the potential energy acquired when they are removed from the solid to infinity. "This relation is strongly reminiscent of a well-known theorem in the theory of radiation, namely, that complete radiation is in equilibrium in any two dielectrics when the energy in a wave-length cube in one is equal to the energy in a wave-length cube of the same frequency in the other. In comparing the energy in the gas to that in the radiation at reasonably low temperatures the corresponding theorem would be, that radiation pressure is in equilibrium with vapour pressure when the energy per molecule capable of evaporating in a wave-length cube residing in the gas is equal to $\frac{25}{8\pi} \sqrt{30\pi} = 0.312$ times the energy residing in a cube of radiation of corresponding wave-length. One may conclude therefore, since the chemical constant can be replaced by radiation pressure, that its physical significance may perhaps be sought rather in the interaction of radiation and matter than in the subdivision of Gibb's N-dimensional space into finite elements of equal probability, [i.e. Planck's assumption, dealt with in Appendix II.]. If these finite cells of equal probability really exist it would seem difficult to escape the conclusion that the atomic heat disappears near the absolute zero. The evidence appears to be against this, as was shown above, and one of the strongest arguments in favour of such a revolutionary assumption would seem to have been removed if the value of the chemical constant can be derived from the radiation pressure."

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